THE NICKEL BULLETIN

A MONTHLY SUMMARY OF CURRENT INFORMATION

NOVEMBER, 1958

CONTENTS

General - - - -	289
Nickel - - - -	290
Electrodeposition and Other Coating Methods -	291
Non-Ferrous Alloys - - -	291 - 292
Cast Iron - - - -	292
Constructional Steels - - -	293
Heat- and Corrosion-Resisting Materials -	294 - 310

(*for details see next page*)

VOLUME 31 NUMBER 11

THE MOND NICKEL COMPANY LTD • THAMES HOUSE, MILLBANK, LONDON, S.W.1
Telephone:- Victoria 3888

INDEX

Page

General

Water Wettability of Nickel and Stainless-Steel Surfaces 289
Tungsten-Arc Cutting Process 289

Nickel

Cleaning of Nickel Crystals by Ion Bombardment 290
Vibrational Spectrum of Nickel Carbonyl 290
Effect of Nickel-Oxide Additions on Adherence of Porcelain Enamel to Steel 290
Effect of Addition of Potash to Nickel-Chromite Catalysts 290

Electrodeposition and Other Coating Methods

Correlation of Structure and Physical Properties of Nickel Electrodeposits 291

Non-Ferrous Alloys

Magnetic Properties and Ordering of Nickel-Manganese Alloys 291
Hydrogenation of Benzene over Copper-Nickel Alloys 291
Nickel Additions to Magnesium and Magnesium-base Alloys 292

Cast Iron

'Ni-Resist': Production and Properties 292

Constructional Steels

Vacuum-Casting Technique for Lowering Hydrogen in Steels 293
Corrosion of Nickel-Copper-Phosphorus Steels in Sea Water 293
Intergranular Oxidation of Chromium-Nickel-Tungsten Steels 293

Heat- and Corrosion-Resisting Materials

The γ' Phase in Nickel-Chromium-base Alloys 294
Thermal Properties of Nickel-containing Materials at Elevated Temperatures 295

Page

Heat- and Corrosion-Resisting Materials (*Contd.*)

Enthalpy and Heat Capacity of 'Inconel' 295
Influence of Alloying Additions on the Stress-Rupture Properties of Nickel-Chromium-Iron-Cobalt Alloys 295
Effect of Atmosphere on Creep-Rupture Properties of Nickel and Nickel-containing Alloys 296
Aeronautical Applications of High-Nickel Alloys 296
Nickel-containing Materials in the 'Gnome' Gas Turbine 297
Tensile, Compressive, Bearing and Shear Properties of Stainless Steel at Elevated Temperatures 297
Oil-Ash Corrosion: Review of Present Knowledge 299
Machining of Stainless-Steel Gas-Turbine Blades 299
Glossary of Terms used in Reference to Corrosion 300
Corrosion-Resistance of Precipitation-Hardenable Stainless Steels 300
Corrosion by Fuming Nitric Acid: Inhibition by Hydrofluoric Acid 301
Behaviour of Steels in Hydrogen-Sulphide Environments 301
Intercrystalline Corrosion of Stainless Steel in Alkaline Solutions 302
Resistance of 'Monel' and Stainless Steel to Corrosion by Sea Water 302
Stainless Steel in Uranium-Refining Plant 303
High-Nickel Alloys in Butane-Isomerization Units 303
Use of 'Monel' in Mercaptan-Extraction Plant 304
Nickel-containing Materials in Plant Producing Phosphoric Acid 304
Use of 'Monel' in Salt-Water Cooling Towers 305
Use of Stainless Steel for Tug Boats and Diesel Railcars 305
Diffusion Bonding of 'Monel' to Copper-Beryllium Alloy 305
Porosity in High-Nickel-Alloy Welds: Causes and Control 306
Welding Chromium-Nickel Austenitic Steels 307
Annealing of Welded Stainless-Steel Tubing 308
Brazing of Cermet Valve Components to 'Inconel' 309

ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

GENERAL

Water Wettability of Nickel and Stainless-Steel Surfaces

D. J. TREVOY and H. JOHNSON: 'The Water Wettability of Metal Surfaces.'

Jnl. Physical Chemistry, 1958, vol. 62, July, pp. 833–7.

It is generally acknowledged that a clean, smooth metal surface should be capable of being well wetted by water and should therefore exhibit zero contact angles, though the quest for such surfaces has not met with much success. The aims of the work described in this paper were twofold: (1) to establish the hydrophilic nature of metal surfaces in general, and (2) to develop a method of producing smooth, clean specimens which, in any investigation of wettability, would provide a means of accurately evaluating the exact nature and amount of contamination involved.

Preparation of specimens by abrasion and solvent rinsing was found not to be satisfactory. The process finally developed involves chemically cleaning the metal with powerful oxidizing acids and subsequent electropolishing to restore smoothness to the etched surfaces. The paper gives full details of techniques suitable for use with aluminium, brass, copper, magnesium, nickel, stainless steel and zinc. By using highly refined handling techniques, low contact angles with water (in the range 0°–11°) were obtained for all these materials.

Tungsten-Arc Cutting Process

R. A. CRESSWELL: 'Development of the Tungsten-Arc Cutting Process.'

Brit. Welding Jnl., 1958, vol. 5, Aug., pp. 346-55.

The paper, which forms a comprehensive review of the development, operation and advantages of the tungsten-arc cutting process, is divided into sections the scope of which is indicated below.

Theory of Arc Cutting

Development of the Tungsten-Arc Process

The section discusses modifications made to the cutting equipment and operational conditions during development of the process. Brief mention is made of cutting tests on aluminium, copper and stainless steel. The lower edge of the cut in stainless steel (and in other materials of relatively high melting point and low thermal conductivity) tended to overheat, causing the metal to run back and bridge the gap behind the arc and also to form droplets on the underside of the workpiece. This problem was overcome by providing extra cooling (e.g., by backing the steel with a copper bar or by water spraying), and by blowing away the droplets by means of an auxiliary jet of fluid.

Equipment,
involving consideration of the power source, torch or cutting head, arc initiation and pilot-arc arrangement, and gas supply.

Cutting Conditions,
for aluminium and its alloys, stainless steel, and copper and its alloys. (Data on cutting speed, arc voltage and shielding gas are given for cutting stainless steel in thicknesses ranging from $\frac{1}{4}$ to 2 in. (0·6 to 5 cm.).)

Profile and Bevel Cutting

Metallurgical Considerations,
which relate specifically to the feasibility of producing welds directly onto the cut edge of a material without need for further preparation. Little or no oxide or nitride film is detectable on the surface of aluminium, and only a very light oxide film on the surface of stainless steel, and it was found that welds can be made on both materials immediately after tungsten-arc cutting. Metallographic examination of such welds, and the results of mechanical tests, proved them to be sound, with properties equivalent to those of welds made on surfaces cut by mechanical methods.

Health Hazards

Review of the precautions necessary during tungsten-arc cutting.

Economic Considerations
involved in cutting aluminium and its alloys are likely to limit the use of the tungsten-arc process to thicknesses in the range $\frac{3}{4}$–2 in. (19–50 mm.). Cutting stainless steel by mechanical methods is difficult : of the two other methods available, arc-cutting has the advantage, over the oxy-acetylene process, of being less complicated, producing little fume, resulting in a readily-weldable surface, and employing cutting speeds some two or three times as fast. It is therefore considered that the tungsten-arc process should prove of both technical and economical value when applied to stainless steel.

NICKEL

Cleaning of Nickel Crystals by Ion Bombardment

H. E. FARNSWORTH, R. E. SCHLIER, T. H. GEORGE and R. M. BURGER: 'Application of the Ion Bombardment Cleaning Method to Titanium, Germanium, Silicon, and Nickel as Determined by Low-Energy Electron Diffraction.'

Jnl. Applied Physics, 1958, vol. 29, Aug., pp. 1150–61.

A method of achieving atomically clean surfaces, comprising a combination of heat-treatment, positive-ion bombardment by an inert gas, and annealing, has been previously described by the authors (*ibid.*, 1955, vol. 26, Feb., pp. 252–3). This paper gives an account of diffraction observations made on titanium, germanium, silicon and nickel crystals cleaned by this technique. To investigate the possibility of contamination from the atmosphere during the cleaning process, tests were carried out on the [100] face of a germanium crystal. Conditions and precautions necessary for effective cleaning are described.

The observed structures were found to be characteristic of atomically clean surfaces. Diffraction studies of the [100], [111] and [110] faces of germanium and of the [100] silicon face indicated that the atomic positions in the surface planes are not the same as the corresponding positions in the bulk structure Results for [100] nickel and [0001] titanium showed the positions of the atoms in the surface planes to be in agreement with X-ray data. With respect to nickel, a double-spaced surface mono-layer and, in some cases, a single-spaced simple-square structure, attributed to diffusion of carbon, were found to be present. Both structures disappeared after several cycles of alternate heating and ion bombardment.

Water Wettability of Nickel and Stainless-Steel Surfaces

See abstract on p. 289.

Vibrational Spectrum of Nickel Carbonyl

L. H. JONES: 'Vibrational Spectrum of Nickel Carbonyl.'

Jnl. Chemical Physics, 1958, vol. 28, June, pp. 1215–19.

The paper presents the results of a study of the infra-red absorption spectrum of nickel carbonyl in the liquid and gaseous states. Assignment of the observed frequencies involved some modification of those previously reported. The most probable assignment of fundamental frequencies appeared to be as follows: 2128 and 381 cm.$^{-1}$ for the A_1 species; 461 and 79 cm.$^{-1}$ for the E species; 2057, 459, 422, 79 cm.$^{-1}$ for the F_2 species; and 300 cm.$^{-1}$ for the F_1 species.

To test the reasonableness of the frequency assignments and to obtain information on the approximate force constants, these values were used to carry out a normal co-ordinate treatment. The results are reported.

Effect of Nickel-Oxide Additions on Adherence of Porcelain Enamel to Steel

J. BERK and J. DE JONG: 'On the Adherence of Porcelain Enamel to Sheet Steel.'

Jnl. Amer. Ceramic Soc., 1958, vol. 41, Aug., pp. 287–93.

Previous investigations had shown conclusively that adherence of enamel to steel could be correlated with roughening of the metal surface during firing. The work described in the present paper was carried out to determine the mechanism responsible for this roughening and, in particular, to establish the rôle of nickel oxide and cobalt oxide in promoting adherence.

Reactions at the interface of the enamel and the low-carbon-steel basis metal were studied, during firing, using enamels with and without small additions of cobalt oxide or nickel oxide.

During the initial stages of firing a layer of oxide appeared on the steel and, at various points on this layer, needles were seen to penetrate the enamel. In the presence of nickel oxide or cobalt oxide small metallic particles were also distinguishable on the iron-oxide layer. X-ray investigation showed that the needles consisted of crystals with the composition $2FeO.SiO_2$. The metallic particles, consisted, in the case of nickel-oxide additions, of a nickel-iron alloy rich in nickel, and, in the presence of cobalt oxide, mainly of iron or an iron-cobalt alloy. Photomicrographs taken during the final stages of firing, after dissolution of the iron-oxide layer, revealed that most of the metallic particles had come into contact with the basis metal and, as a result of an atomic diffusion process at the points of contact, had adhered to it. As firing continued, roughening of the basis metal occurred; this effect is attributed to the growth of the metallic particles which had adhered to the surface, and to pitting of the basis metal in the vicinity of the particles. Precipitation of the metallic particles on the oxide layer and roughening of the basis metal are both explained in terms of electrochemical mechanisms.

The authors use their findings as a basis for a short discussion of ways in which enamels may adhere to steel.

Effect of Addition of Potash to Nickel-Chromite Catalysts

H. C. ROWLINSON: 'The Effect of Addition of Potash to Nickel–Chromite Catalysts.'

Canad. Jnl. Chemistry, 1958, vol. 36, July, pp. 1053–6.

The work reported in this paper represents part of a wider study of olefin dehydrogenation catalysts containing nickel chromite. It was carried out (1) to study the effect of potash additions on the performance of a nickel-chromite catalyst used for the dehydrogenation of butene-1 in the presence of steam at 600°C., and (2) to determine the relative effectiveness of adding the potash (about 10 wt. per cent.) directly to the catalyst during its preparation,

or of addition (about 0·125 wt. per cent.) by impregnation from solution. An unpromoted nickel-chromite catalyst was used as a control, and the efficiency of the three catalysts was estimated from the mole percentage of butene decomposed and the mole percentage of the decomposed butene converted to butadiene.

The main effect of the potash was to eliminate the tendency to wildness which was exhibited by the pure nickel-chromite catalyst, and so to improve selectivity to butadiene. This effect is attributed to its preventing reduction of nickel oxide to the metallic particles of nickel which act as a disruptive catalyst.

The behaviour of the catalyst to which the potash had been directly added differed from the impregnated catalyst in two respects: it suffered considerable lay-down of carbon, and, in the initial half-hour of activity, its behaviour for a time resembled a 'wild' condition, until a stable conversion, approximately equivalent to that of the impregnated catalyst, was achieved. This variation in performance is attributed to the formation of a network of pores in the catalyst due to reduction of the dispersed potassium chromate. The butene decomposes to carbon because the butadiene cannot diffuse out. When the pores become filled with carbon the behaviour of the catalyst resembles that of a surface-promoted type.

Hydrogenation of Benzene over Nickel and Copper-Nickel Alloys

See abstract in right-hand column.

ELECTRODEPOSITION AND OTHER COATING METHODS

Correlation of Structure and Physical Properties of Nickel Electrodeposits

D. J. EVANS: 'The Structure of Nickel Electrodeposits in Relation to Some Physical Properties.'

Trans. Faraday Soc., 1958, vol. 54, July, pp. 1086–91.

The structure of electrodeposits has been the subjec of much research, but the basic problem of the cause of the various preferred orientations remains as yet unexplained, and relatively little attention has been paid to relationships which might exist between the structure and physical properties of the deposit. On the assumption that determination of such relationships would throw light on the factors involved, the author sought some correlation between preferred orientation, internal stress, grain size, surface appearance and hardness of nickel deposits produced, at various temperatures, from five different plating solutions. Compositions of the electrolytes are tabulated and test procedures described.

The predominant orientations in matt, semi-bright and bright deposits were found to be either [100] or [110] or a mixture of both, and for any given electrolyte the [110] orientation was shown to be associated with the higher values of internal stress and hardness; use of higher deposition temperatures, corresponding to a decrease in internal stress and hardness, produced the [100] texture. Suggestions that brightness could be correlated with either a high degree of orientation or a grain size smaller than the wave length of light were not substantiated by the present results; no connexion was found between brightness and orientation, and the grain sizes of matt, semi-bright and bright nickel deposits were similar. Brightness appeared to be the result of a smoothing action during the formation of the deposits, the free surface of the grains being flat and parallel to the general surface direction of the specimen: the fact that the deposits also showed a high degree of preferred orientation is incidental to, and not the cause of, the brightness.

NON-FERROUS ALLOYS

Magnetic Properties and Ordering of Nickel-Manganese Alloys

R. HAHN and E. KNELLER: 'Magnetic Properties and Order Structure of Nickel-Manganese Alloys. I. Quasiparamagnetism of Partially-Ordered Nickel-Manganese Alloys.'

Zeitsch. f. Metallkunde, 1958, vol. 49, Aug., pp. 426–41.

With the aim of determining the relationship between the magnetic behaviour and structure of partially ordered alloys, the authors investigated variations in the magnetic and electrical properties of nickel-manganese alloys (containing 20–35 at. per cent. of manganese) as a function of ordering during isothermal treatment. Determination of this relationship would, it was expected, provide a means of acquiring, by measurement of magnetic properties, data hitherto unobtainable on the ordering mechanism and structure of partially ordered alloys.

The results of the investigation are reported in detail. In discussion of the data, reference is made to a *bibliography* of 51 items.

Hydrogenation of Benzene over Copper-Nickel Alloys

W. K. HALL and P. H. EMMETT: 'The Hydrogenation of Benzene over Copper-Nickel Alloys.'

Jnl. Physical Chemistry, 1958, vol. 62, July, pp. 816–21.

In connexion with the hydrogenation of benzene over copper-nickel alloys, various studies have been made correlating catalytic activity with the electronic properties of the solid state. The present paper is concerned with a kinetic study of hydrogenation of benzene over eleven catalysts (ranging in composition

from pure nickel to pure copper) and was carried out to obtain data, on absolute activities and activation energies, which would serve as a basis for assessment of the various theories advanced to explain the relationship.

As was anticipated from the results of previous work, the isothermal-activity data exhibited a sharp decrease near the critical composition (60 per cent. copper, 40 per cent. nickel), where the *d*-band of the metal is just filled. Activation-energy data indicated, however, that the changes observed in activity did not reflect changes in the activation energies, but resulted from overpowering 'compensations' by the frequency factors. An interpretation of these results is suggested.

Influence of Nickel Additions on Properties of Magnesium and Magnesium-base Alloys

R. R. NASH, H. K. ADAMS, A. E. BIBB, M. C. HUFFSTUTLER and E. J. TULLOCH: 'Magnesium Alloys with High Melting Point Additions.'

Wright Air Development Center, Tech. Report 55-207, Mar. 1957; 180 pp. *P.B.* 131198.

The investigation described in the report was carried out to determine the effect, on the physical and mechanical properties of magnesium and selected magnesium-base alloys, of alloying additions of the following metals: titanium, hafnium, rhenium, yttrium, nickel, cobalt, tantalum, chromium, vanadium, niobium, boron, tungsten and molybdenum. The work was exploratory and part of a wider study, the ultimate aim of which was the development of wrought magnesium-base alloys with improved properties *vis-à-vis* those of current commercial alloys.

The results are presented *in extenso*, in sections relating to each of the addition metals investigated. The effectiveness of the individual alloying elements was assessed, and is discussed, on the basis of the results of work reported in the literature, the ease with which the alloying addition could be introduced, its grain-refining effect, the degree of solid-solubility attained, and the influence of the element on mechanical properties and corrosion-resistance.

The results indicate that the solubility in magnesium of titanium, hafnium, vanadium, boron, chromium, niobium, tungsten and molybdenum is extremely limited, and addition of these elements was found to have little effect on either the mechanical properties or corrosion-resistance of the resultant alloys. Excellent corrosion-resistance was, however, achieved in certain magnesium-rhenium and magnesium-tantalum alloys, while additions of yttrium significantly improved room-temperature mechanical properties. Titanium dioxide and vanadium were found to be effective grain refiners.

Nickel and cobalt both exhibited limited solid solubility in magnesium and magnesium-base alloys. Nickel additions resulted in some refinement of the as-cast grain structure and achieved a moderate increase in room- and elevated-temperature mechanical properties of hot-rolled sheet; their effect on resistance to corrosion was, however, deleterious.

CAST IRON

Production and Properties of 'Ni-Resist'

R. BARTON: 'Constitution, Production and Mechanical Properties of 'Ni-Resist'.'

Brit. Cast Iron Research Assocn., Jnl. Research and Development, 1958, vol. 7, Aug., pp. 299-315; *Research Report* 488.

The report comprises a concise but comprehensive survey of the composition, constitution and mechanical properties of the high-nickel-alloy cast irons known by the generic name of 'Ni-Resist', and of the production technique suitable for irons of that type. Details are given of the compositions of the eight grades, and of the specific types of service for which the respective varieties have been developed. Nickel content ranges from 13·5 to 36 per cent., with or without varying amounts of copper and/or chromium.

The scope of the material contained in the report, which is derived from independent tests made in the laboratories of the British Cast Iron Research Association as well as from published literature, is indicated below.

Constitution and Structure. Typical T.T.T. curves are presented to illustrate the influence of alloying, on the M_s temperature of the irons, and to demonstrate the achievement of a stable austenitic structure. The influence of each of the constituent elements is discussed in relation to constitution, and typical microstructures are illustrated.

Properties. Data on thermal, electrical and magnetic properties are tabulated, and the following mechanical properties are discussed, in relation to composition: tensile, compressive, transverse and torsional strengths; hardness; impact-resistance; elevated-temperature mechanical properties; creep-resistance; fatigue strength; heat-resistance.

Founding. Procedures used in the production of the high-alloy cast irons are outlined, with discussion of suitable melting furnaces, the methods of control necessary for production of cupola-melted iron, means employed for introduction of the alloying elements, and general foundry technique.

Machining Practice. Attention is directed to precautions required in view of the tendency of 'Ni-Resist' cast irons to work-harden. Recommendations are made with regard to cutting speeds and feeds.

Corrosion-Resistance. The corrosion-resisting characteristics of the 'Ni-Resist' irons are reviewed in relation to the behaviour of such materials in contact with mineral acids, organic acids, alkalis, salt solutions, and water.

Applications. The report ends with a brief review of some of the uses for which 'Ni-Resist' irons have proved suitable. *Inter alia*, reference is made to

furnace castings and other heat-resisting parts, castings used in service involving corrosive attack, bearings, and cylinder liners.

The report includes a considerable amount of reference information.

CONSTRUCTIONAL STEELS

Vacuum-Casting Technique for Lowering the Hydrogen Content of Steels

J. N. HORNAK and M. A. OREHOSKI: 'Vacuum Casting of Steel.'

Jnl. of Metals, 1958, vol. 10, July, pp. 471–5.

Investigations carried out over a number of years by the U.S. Steel Corporation had indicated that with normal casting practices, even under ideal conditions, the hydrogen content of steel was unlikely to be lower than about 2 p.p.m. It was believed, however, that in large steel forgings the maximum hydrogen content compatible with satisfactory resistance to flaking and to hydrogen embrittlement was 1·15 p.p.m.; the authors' attention was therefore transferred to the feasibility of developing a vacuum-casting process which would reduce the hydrogen content to this level as a maximum. A preliminary survey in this connexion revealed four main problems: (1) casting pressures would need to be substantially lower than those previously used; (2) the pumping capacity required would therefore be greater than normal; (3) the costs of such pumping equipment would be very high; (4) control of the pouring stream would be difficult. This paper gives details of the investigations involved in the solution of these problems, describes the equipment and procedure which were finally developed, and presents the results of analyses of steels before and after vacuum casting.

The data, (tabulated for the hydrogen, oxygen and nitrogen contents of nickel-molybdenum-vanadium, nickel - chromium - molybdenum - vanadium, nickel-chromium-molybdenum, nickel-molybdenum-vanadium, manganese-nickel-molybdenum-vanadium, and chromium-molybdenum-vanadium steels in various ingot sizes), show that hydrogen contents ranged from 3 to 6 p.p.m. before, and from 0·3 to 2·0 p.p.m. after, vacuum casting. The steel exhibited no tendency to flaking and the ductility of vacuum-cast specimens was found to be similar, irrespective of whether they had been aged or not.

Corrosion of Nickel-Copper-Phosphorus Steels in Sea Water

C. P. LARRABEE: 'Corrosion-Resistant Experimental Steels for Marine Applications.'

Nat. Assocn. Corrosion Engineers, 14*th Annual Conference*, Mar. 1958, *Preprint*; 7 pp.+ figures.

The corrosion of carbon-steel piles used in sea-water installations has been found to be most severe in the 'splash zone'. Previous investigations had indicated that low-alloy nickel-copper-phosphorus steels exhibited higher corrosion-resistance under these conditions: the data presented in this paper were derived from corrosion tests carried out with the aim of comparing the two materials in this respect.

Specimens of carbon steel (piling) and nickel-copper-phosphorus steels were exposed in sea water, so that one end of the specimen extended above the splash zone and the other was in the harbour mud. Six grades of the alloy steel were used: their compositions and tensile properties are given. The specimens, which were 20 ft. (6 m.) long and 6 in. (15 cm.) wide, were removed for examination after exposure for one, two or five years. Corrosion-resistance was assessed on the basis of loss in weight and decrease in thickness. In further tests specimens of the two types of steel were exposed, together with a copper structural steel, to a severely corrosive marine atmosphere for 0·5, 1·5 or 3·5 years.

The results of the sea-water tests are regarded as conclusive evidence that the nickel-copper-phosphorus steels are, as a class, much more resistant than the carbon steel to the particular splash-zone conditions represented by the tests. Of the six alloy steels investigated, best results were obtained with that containing nickel 0·5, copper 0·5, phosphorus 0·12, per cent.: the resistance of this steel to pitting was at least three times as great as that of the carbon steel. Corrosion below the low-tide line was not significantly influenced by composition: the corrosion rate was about 4·5 mils per year.

The superiority of the nickel-copper-phosphorus steels (*vis-à-vis* the carbon steel) was further emphasized by the results of the atmospheric corrosion tests. During the last two years of a 3½-year test, the weight loss of the most resistant nickel-copper-phosphorus steel was only 5 per cent. of that of the carbon steel.

Investigation of a 0·5/0·2/0·12 nickel-copper-phosphorus steel is continuing.

Intergranular Oxidation of Chromium-Nickel-Tungsten Steels

P. CSOKÁN: 'Intergranular Oxidation of Chromium-Nickel-Tungsten Steels.'

Metalloberfläche, 1958, vol. 12, Aug., pp. 230–2.

The investigation described by the author originated in the premature fatigue failure of a machine component fabricated from a chromium-nickel-tungsten steel of composition: carbon 0·22, silicon 0·17, manganese 0·35, sulphur 0·020, phosphorus 0·021, nickel 4·05, chromium 1·4, tungsten 1·02, per cent. The component, which during operation was required to withstand severe dynamic stressing, had been hardened and tempered by heating for 30 minutes in the range 860°–880°C., oil-quenching, reheating for 30 minutes at 200°C. and air-cooling.

Metallographic examination of a hairline crack, associated with the failure, showed that in the area bordering the surface there were signs of decarburization; along the primary grain boundaries in this

decarburized region there was distinguishable a light-coloured network which had obviously formed the path of the crack in its initial stages. (Photomicrographs illustrating these phenomena are included in the paper.) In an effort to determine the cause of the intergranular light-coloured phase, tests were carried out to establish at what stage in the heat-treatment it occurred. By variation of the hardening conditions it was found that heating in an air-free atmosphere produced no decarburization in the steel; heating in an open furnace, on the other hand, resulted in the formation of a decarburized surface layer (the thickness of which was governed by the time of heating), severe scaling and intercrystalline oxidation. Exposure of the steel to a slightly oxidizing atmosphere produced a surface layer which was only partially decarburized, but in which could be seen a light-coloured network similar to that in the defective component. In further tests, steels containing 2 per cent. of chromium, 2 per cent of nickel and 2 per cent. of tungsten were heated at 860°C. for four hours in a slightly oxidizing atmosphere: a similar decarburized network was obtained.

It is suggested, as a possible mechanism, that where the diffusion rate of the oxygen is less than that of the carbon, the surface layer of the steel will be decarburized; if however, the diffusion rates are reversed, the excess oxygen will oxidize both iron and carbon, and result in severe scaling.

Occurrence of the heterogeneous intercrystalline phase in the chromium-nickel-tungsten-steel component was prevented by copper-plating the component prior to heat-treatment. In a slightly oxidizing furnace atmosphere the coating is oxidized to copper oxide, while the steel itself remains unaffected. After hardening, the coating is easily removed by pickling in appropriately inhibited acid pickling solution. Elimination of the intercrystalline phase also eradicated any tendency to premature fatigue failure.

HEAT- AND CORROSION-RESISTING MATERIALS

The γ' Phase in Nickel-Chromium-base Alloys

J. A. AMY and W. C. BIGELOW: 'Crystallographic Structure and Orientation of the γ' Phase in Four Commercial Nickel-base Alloys.'

Wright Air Development Center, Tech. Note 57-247, July 1957; 12 pp. *P.B.* 131518.

It has been demonstrated in many investigations that the age-hardening characteristics of nickel-base alloys containing titanium and aluminium are the result of the presence of the time- and temperature-dependent precipitation of the intermetallic γ' phase. X-ray diffraction results have shown that in a number of the simple alloys of this type the γ' phase has an ordered face-centred-cubic structure based on that of the Ni_3Al phase of the nickel-aluminium system, with a lattice parameter usually in the range 3·55 to 3·60 Å units, and therefore very nearly the same as that of the γ (face-centred-cubic) matrix phase. Attempts to apply X-ray methods to the more complex commercial alloys have in many cases been unsuccessful, due, apparently, to the fact that some of the additional alloying elements enter substitutionally into the γ' structure, causing a reduction in the intensities of the superlattice reflections and, in some cases, causing the lattice parameter to become almost identical with that of the matrix phase.

In the work described in this report the extraction-replica technique developed by FISHER (*A.S.T.M. Special Tech. Publn. No.* 55, 1953, p. 49) was used to provide electron-diffraction patterns from the matrix precipitate particles. The essential features of this process are briefly summarized.

The alloys examined were four commercial nickel-base types ('Inconel X', 'Waspalloy', 'M-252' and 'Udimet'), all of which contain titanium and aluminium as hardening agents. From the patterns obtained, the matrix particles were conclusively identified as the γ' phase, and it was shown also that the ordered, or superlattice, structure reported as characteristic of this phase in simpler alloy systems occurs also in the complex alloys and that the particles develop with a high degree of preferred crystallographic orientation relative to the matrix lattice. Variations observed in the size, shape and distribution of the particles, in specimens of the four alloys aged for 100 hours at 1400°F. (760°C.), appear to be related to the titanium and aluminium contents.

R. F. WILDE and N. J. GRANT: 'Ageing in Complex Commercial Ni-Cr Alloys Hardened with Titanium and Aluminium.'

Trans. Metallurgical Soc., Amer. Inst. Mining and Metallurgical Engineers, 1958, vol. 212, June, pp. 417-19.

Discussion, by W. C. BIGELOW and J. A. AMY and by H. J. BEATTIE and W. C. HAGEL, on the above paper (*Trans. Amer. Inst. Mining and Metallurgical Engineers*, 1957, vol. 209, pp. 865-72: see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 10, p. 185).

Contributions to the discussion were concerned mainly with the occurrence of the γ' phase in the nickel-chromium-molybdenum alloy 'M-252' and with the nature of the carbides present in four typical nickel-chromium-base alloys of varying composition.

J. R. MIHALISIN: 'The Selective Identification of Constituents in 'Nimonic 80' by Extraction-Replica Technique', *ibid.*, pp. 349-50.

This note reports application of the extraction-replica technique to isolation and examination of a cellular or discontinuous precipitate sometimes observed in the nickel-chromium-aluminium-titanium alloy 'Nimonic 80'. Details of etching media and procedure are given. The precipitate was identified as an $M_{23}C_6$ type of carbide, having a lattice parameter almost identical with that of $Cr_{23}C_6$. Formation of this precipitate, which deleteriously affects ductility at high temperatures, can be avoided by suitable heat-treatment.

Thermal Properties of Nickel-containing Materials at Elevated Temperatures

I. B. FIELDHOUSE, J. C. HEDGE, J. L. LANG and T. E. WATERMAN: 'Thermal Properties of High-Temperature Materials.'
Wright Air Development Center, Tech. Report 57-487, Feb. 1958; 79 pp. *P.B.* 131718.

The thermal conductivity, specific heat and linear coefficient of thermal expansion of the following heat-resisting materials have been determined over the temperature range 1000°–3000°F. (540°–1650°C.):

(1) Silicon carbide,
(2) 'Stellite 21' (cobalt-chromium-molybdenum-nickel alloy),
(3) 'Hastelloy B' (nickel-molybdenum-iron alloy),
(4) 'Hastelloy C' (nickel-molybdenum-chromium-iron-tungsten alloy),
(5) '17-7 P.H.' (chromium-nickel precipitation-hardenable stainless steel),
(6) A.I.S.I. Type 446 stainless steel (a straight-chromium grade),
(7) 60-15 Cr' (nickel-chromium-iron alloy),
(8) Beryllium.

The report is divided into three sections: each gives full details of apparatus and procedure used in, and presents the data obtained from, measurement of the property for which values are given.

Enthalpy and Heat Capacity of 'Inconel'

T. B. DOUGLAS and A. W. HARMAN: 'Enthalpy and Heat Capacity from 0° to 900°C. of Three Nickel-Chromium-Iron Alloys of Different Carbon Contents.' *Jnl. Research, Nat. Bur. Standards*, 1958, vol. 60, June, pp. 563-8; *R.P.* 2870.

The work described formed part of a test programme designed to provide data which would facilitate investigation of the factors involved in aerodynamic heating of structural materials used in supersonic aircraft and missiles. The relevant properties were determined for 'Inconel' (a nickel-chromium-iron alloy), selected for investigation as typical of the materials used in such applications. The alloy was examined at three levels of carbon content (0·02, 0·07 and 0·11). Measurements relating to specific heat, thermal conductivity, thermal expansion, electrical resistance and emissivity were reported by O'SULLIVAN (see *Proc. Amer. Soc. Testing Materials*, 1955, vol. 55, pp. 757-63; *Nickel Bulletin*, 1956, vol. 29, No. 8-9, p. 170); data on enthalpy and heat capacity are presented by the present authors.

Enthalpy relative to 0°C. was measured, at intervals of 100°, over the range 100°–900°C. The influence of heat-treatment and hardness was assessed by determination at 600°C. of the enthalpies of specimens of the 0·07 per cent. carbon alloy in various conditions of heat-treatment.

Data on enthalpy are presented in tabular, and heat capacities in graphical, form. Heat-capacity/temperature curves for the three 'Inconel' alloys were almost identical. They differ, however, from the smooth curves characteristic of the simplest crystalline materials in one significant respect: within the temperature range 500°–600°C. the heat capacity of the alloys rapidly increased to a value 3–5 per cent. greater than that which would be obtained by extrapolation from values at lower temperatures. This behaviour suggests that the materials undergo some type of transition which is accompanied by change in physical properties. (Anomalies in the thermal expansion, electrical resistivity and ultimate and yield strengths of the same alloys have been reported to occur in approximately the same range of temperature.)

Equations are presented by means of which the enthalpy of the alloys relative to 0°C. may be calculated, in absolute joules per gram, for any desired temperature in the range investigated.

Influence of Alloying Additions on the Stress-Rupture Properties of Nickel-Chromium-Iron-Cobalt Alloys

J. H. SYE, T. L. ROBERTSHAW and F. M. RICHMOND: 'Investigation of the Effects of Incongruous Elements and the Interaction Effects of these Elements on High-Temperature Strength of Fe-Co-Ni-Cr Alloys.'
Wright Air Development Center, Tech. Report 57-426, Dec. 1957; 102 pp. *P.B.* 131614.

The report is the second describing the results of an investigation to determine the influence of various combinations of alloying additions on the stress-rupture properties of vacuum-melted alloys of the following base composition: nickel 60, chromium 20, iron 10, cobalt 10, at. per cent. The results of previous tests (presented by ROBERTSHAW and RICHMOND as *W.A.D.C. Tech. Report* 56-114) indicated that stress-rupture properties, based on tests at 1600°F. (870°C.), were influenced to a great extent by the vacuum attained during melting, the method of fabrication and the total hardener content. Assessed on the basis of atomic misfit, the increase in rupture strength achieved by addition of boron, zirconium and niobium was equivalent to that obtained by molybdenum. Titanium was found to be more, and aluminium less, effective in this respect than molybdenum.

The aims of the present investigation are summarized as follows:

'1. To obtain comparable results at 1300°F. (705°C.) for the same alloys (2nd series).
'2. To investigate addition of aluminium, titanium, and molybdenum, in large amounts, and boron, zirconium and carbon, in small amounts (3rd series).
'3. To attempt to establish composition and conditions giving optimum properties, in a basis alloy derived from the preceding group, with smaller changes in the amounts of aluminium, titanium and molybdenum (4th series). Rupture tests were conducted at 1800°F. (980°C.) for cast material and 1750°F. (955°C.) for wrought material.
'4. To investigate the substitution of tantalum for molybdenum in the 4th series (5th series).

'5. To investigate the substitution of tungsten for the molybdenum in the 4th series (6th series).
'6. To analyse the results of balanced experiments and to design 'better' alloys therefrom.'

All heats studied were melted and cast *in vacuo*, by methods normally used for commercial nickel-base alloys. (The composition of each is tabulated.) The test programme involved:

(1) High-strain-rate tensile tests on as-cast material, as a means of determining the optimum forging temperature.
(2) Stress-rupture tests on cast and forged material in the heat-treated condition.
(3) Tests carried out in an atmosphere of moving air, to determine oxidation-resistance at 1800°F. (980°C.).
(4) Slow-strain-rate tensile tests, at room and elevated temperature, on cast and forged material in the heat-treated condition.

The value and limitations of the balanced experimental designs used in the later phases of the investigation are discussed. The paper includes photomicrographs of each of the series of alloys and the test data obtained are presented in detail. The conclusions drawn by the authors are given below.

'1. The response of alloys to the addition of hardening elements depended on the test temperature used.
'2. In the alloy system containing aluminium, titanium and molybdenum as hardeners, strong interactions were noted between these elements.
'3. In the alloy system containing aluminium, titanium and tantalum as hardeners a strongly negative tantalum-titanium interaction was important.
'4. In the alloy system containing aluminium, titanium and tungsten as hardeners a negative aluminium-titanium interaction was significant.
'5. A stress-rupture life of about 135 hours at 1800°F. (980°C.) and 15,000 p.s.i. (6·5 t.s.i.; 10·5 kg./mm.²) was achieved in an alloy of the following nominal composition: nickel 49, chromium 14, tungsten 12, iron 8·5, cobalt 8·5, aluminium 4·2, titanium 3·7, carbon 0·2, boron 0·002, zirconium 0·04, per cent.
'6. A rupture life of 149·1 hours at 1750°F. (955°C.) and 15,000 p.s.i. (6·5 t.s.i.; 10·5 kg./mm.²) was achieved in a wrought alloy of the following nominal composition: nickel 50, chromium 14·5, tungsten 11·5, iron 8·5, cobalt 8·0, aluminium 4·4, titanium 2·0, carbon 0·15, boron 0·002 and zirconium 0·09, per cent.
'7. Alloys capable of being tested in both the wrought and the cast conditions exhibited comparable stress-rupture results.'

Effect of Atmosphere on Creep-Rupture Properties of Nickel and Nickel-containing Alloys

P. SHAHINIAN and M. R. ACHTER: 'Effect of Environment on Creep-Rupture Properties of Metals.'
Report of U.S. Naval Research Laboratory Progress, 1958, Apr., pp. 18–24.

The report summarizes the results of an extensive investigation of the influence of environment on the creep properties of metals and alloys. Creep rate and rupture life were determined, in air and *in vacuo*, at temperatures ranging from 1100° to 1900°F. (595° to 1035°C.), for the following materials (selected with the aim of evaluating the influence of the two environments in terms of composition, oxidation-resistance and ductility): nickel, 'Nichrome V' (an 80–20 nickel-chromium alloy), and a relatively brittle alloy containing nickel 76, chromium 20, aluminium 4, per cent. The results of the tests on the nickel and 'Nichrome V' have been published separately (see abstracts in *Nickel Bulletin*, 1958, vol. 31, No. 6, p. 157; No. 2, p. 50); those relating to tests on the nickel-chromium-aluminium alloy will be published later as *U.S. Naval Research Laboratory Report* 5133.

From investigation of the creep properties of the nickel and 'Nichrome V' it was concluded that the influence of atmosphere was affected by temperature and the rate of strain to which the specimen was subjected. At low rates of strain and high temperatures the strength of the material was higher in air than *in vacuo*; at high strain rates and low temperatures the position was reversed. Moreover, a reversal in the relative creep strengths occurred during the tests. In the early stages the specimen tested in air had the better creep-resistance: at a later stage the resistance of the vacuum-tested material was the higher. The rupture life of the aluminium-modified alloy was found to be similarly influenced by environment, but, unlike those of the other materials tested, its minimum creep rate was unaffected. This difference in behaviour is explained, as follows, in terms of the mechanism proposed to account for the effects of environment (i.e., that oxidation strengthens the material, but that adsorption of gases weakens it by lowering surface energy and thereby facilitating crack propagation).

'In contrast to the more ductile nickel, in which crack initiation and growth were observed through the second stage of creep, cracking in the aluminium-modified alloy was found to be approximately coincident with entry into the third stage. The minimum creep rate was therefore measured, in the case of nickel, while cracking was taking place, whereas for the alloy it occurred before cracking started. Since environment influences ease of crack propagation, the minimum creep rate of the nickel is affected by the atmosphere, but not that of the alloy. Thus, although the same mechanism applies to all three materials, an important difference is that the influence of environment is observed in a later stage for the relatively brittle aluminium-containing alloy.'

Aeronautical Applications of High-Nickel Alloys

HENRY WIGGIN & CO. LTD.: 'Wiggin Nickel Alloys in Aircraft.'
Publn. 1114A,* 1958; 62 pp.

The first half century in the history of aeronautical engineering has seen advances unpredictable by the

* *We shall be pleased to supply a free copy of this publication.*

early pioneers, and the evolution of the gas-turbine engine has now provided the industry with further incentive for development. Each step forward has brought demands for improvements in materials of construction. New alloys are required to meet increasingly exacting specifications, and new forms of existing alloys are needed to meet a widening range of uses. This publication reviews the properties of high-nickel alloys produced by Henry Wiggin and Company, Ltd., and their uses in the aircraft industry.

The review is divided into sections, each of which relates to the alloys of a particular series. Information on aeronautical applications is supplemented by many illustrations of typical components. The scope of the sections is outlined below.

'*Nimonic*' *Series*

These alloys were developed specifically for the rotor blading of British aircraft gas turbines, and have not only remained the standard material for this application over a period of 17 years, but have also been adopted for a wide range of other heat-resisting applications in aircraft. Notes are given on the use of 'Nimonic' alloys for turbine rotor blades, turbine stator blades, turbine discs, flame tubes, afterburners, exhaust units, gas-turbine rings, rocket motors, ramjets, and helicopter rotor-tip jets.

'*Nimocast*' *Series*

Introduced to meet the need for a range of casting alloys with good high-temperature properties, these materials are of nickel-chromium base and are related to the wrought alloys of the 'Nimonic' series. 'Nimocast' 75, 80, and 90 are, for example, the casting equivalents of similarly-numbered alloys in the 'Nimonic' series. Applications discussed are: turbine stator blades, rotor blades, discs, and rings.

'*Inconel*'

Of nominal composition nickel 76, chromium 15, iron 8, per cent., 'Inconel' combines excellent resistance to high-temperature oxidation with a high resistance to many types of corrosion, and has proved its value for long service under exacting conditions. Applications: exhaust manifolds, turbo-blower casings, ramjets.

'*Monel*'

The excellent corrosion-resistance, mechanical properties and ease of fabrication of this nickel-copper alloy are utilized to advantage in the following components: air-frame rivets and fasteners, filtration equipment, anti-vibration mountings, hydraulic pipelines, de-icing systems.

'*K Monel*'

This alloy contains small percentages of aluminium, which render it age-hardenable; the effects of work-hardening can be combined with those of heat-treatment to produce an alloy which possesses the strength and hardness of an alloy steel and the outstanding corrosion-resistance of standard 'Monel'. Uses reviewed are: air-frame rivets and bolts, electrically operated hydraulic valves, fuselage skin.

Nickel

is included among the materials reviewed mainly on account of its use in thermionic valves.

'*Brightray*' *Series*

The nickel-chromium and nickel-chromium-iron electrical-resistance alloys of this series are used in a wide variety of equipment installed in aircraft (e.g., for de-icing and fire detection).

'*Nilo*' *Series*

Used where controlled low coefficients of thermal expansion are essential (e.g., in glass-to-metal seals and high-energy ignition plugs).

The publication also contains brief notes on the aeronautical applications of 'Ferry', 'Ni-Span C', the 'Mangonic' alloys and 'Thermometals'.

Nickel-containing Materials in the 'Gnome' Gas Turbine

'Introducing the 'Gnome'.'

Aeroplane, 1958, vol. 95, Aug. 15, pp. 225–8.

The 'Gnome D.Ge.1' free-turbine engine, due to make its first run in March of next year, is expected to be the first British-built unit to meet the need for a 1000-s.h.p. shaft-turbine engine suitable for use both in helicopters and (in a modified turbo-prop version) in fixed-wing aircraft. It is being manufactured by the de Havilland Engine Company, Ltd., on licence from the General Electric Company, Ltd. As the American 'T-58', it passed its type-test in Oct. 1957 and has since found increasing application in the United States in both rotary- and fixed-wing aircraft. It will be available in single or coupled form. The 'Gnome', although only 5 ft. (1·5 m.) long and 1½ ft. (0·45 m.) wide has a power/weight ratio as high as 2·86/1, and is expected eventually to be capable of producing 1500 s.h.p.

This article gives details (illustrated with cut-away diagram) of the engine's design and main components. Many of the major parts are manufactured in high-nickel alloys: reference is made, for example, to the use of 'Nimonic 90' or 'Nimonic 80A' for the turbine blades, and of 'Nimonic 75' for the flame tube of the combustion chamber, turbine shrouding, the inter-turbine seal and the exhaust-duct casing.

Tensile, Compressive, Bearing and Shear Properties of Stainless Steel at Elevated Temperatures

J. V. MELONAS and J. R. KATTUS: 'Determination of Tensile, Compressive, Bearing, and Shear Properties of Ferrous and Non-Ferrous Structural Sheet Metals at Elevated Temperatures.'

Wright Air Development Center, Tech. Report 56-340, Sept. 1957; 282 pp. *P.B.* 131461.

The investigations described in the reports to which this and the following abstracts relate fall within the scope of an extensive research programme, initiated with two purposes: (1) to determine design data for materials used, in the form of sheet, for aircraft structures; (2) to establish some relationship, between the tensile properties and the compressive, bearing

and shear properties of the materials, which would provide a means of predicting other mechanical properties from tensile data alone.

Design data based on mechanical properties derived from high-temperature tests, using the standard exposure time of 30 minutes, are not necessarily applicable to aircraft materials intended for service involving long-time exposure at high temperatures. To provide data which would be relevant to the actual service conditions, properties of typical materials of construction were determined after exposure times of up to 1000 hours at the test temperature: this phase of the investigation is described in the present report.

Four materials were investigated: a low-alloy chromium-molybdenum steel, a titanium alloy, a magnesium alloy, and an 18–8 (A.I.S.I. Type 301) chromium-nickel stainless steel. Properties determined are given below.

Tensile Properties

Ultimate strength;
Rupture strength;
Yield strength (0·2 per cent. offset);
Modulus of elasticity.

Compressive Properties

Tangent modulus;
Modulus of elasticity;
Yield strength (0·2 per cent. offset).

Bearing Properties

Ultimate strength;
Yield strength.

Shear Properties

Ultimate shear strength.

The stainless steel was tested, in the full-hard condition, in the form of sheet 0·045-in. (1·125 mm.) thick, at 75°, 200°, 400°, 600°, 800° and 1000°F. (25°, 95°, 205°, 315°, 425° and 535°C.) after being held at the test temperature for ½, 2, 10, 100 and 1000 hours. The stainless steel was not available in the sheet thickness from which the shear specimens were machined and shear properties for this material were therefore not determined. Full particulars are given of test specimens, apparatus and procedure used in the investigation. The data obtained are presented *in extenso*.

The effects of variations in temperature were found, in general, to be greater than those of varying time at temperature. The strength and modulus properties of all the materials decreased to some degree with rise in temperature over the range studied. Increase in exposure time, which did not significantly influence values for modulus of elasticity, resulted, at the higher temperatures, in some decrease in strength properties, but had little effect at the lower temperatures.

Results for the stainless steel showed that, in general, the tensile and bearing strength decreased to levels between 50 and 70 per cent. of the room-temperature values as the temperature was raised from 75 to 1000°F. (from 25° to 535°C.). At 1000°F. (535°C.) the compressive yield strength was between 75 and 85 per cent. of the value obtained at room temperature. Tensile and compressive moduli of elasticity were not greatly affected by rise in temperature: at 1000°F. the values for these properties were between 80 and 92 per cent. of the room-temperature levels. At 400° and 600°F. the tensile post-yield stress-strain curves showed sharp downward discontinuities shortly before rupture, but at the other test temperatures the curves were smooth and continuous. Variations in exposure time had no consistent effect on the tangent-modulus curves for the steel. Tensile elongation was uniformly low and not appreciably affected by changes in exposure time. Elongation was greater at room temperature than at any of the other test temperatures.

Consideration of the various properties determined showed that their relationship varied with differences in composition, temperature and exposure time, and it is concluded that reliable data on such properties can be obtained only by testing under the service conditions. The relationships which were established could, however, be used to obtain some indication of one property from data pertaining to another. The accuracy of these calculations ranged from ±11 to ±55 per cent.

See also

D. E. MILLER: 'Determination of the Tensile, Compressive and Bearing Properties of Ferrous and Non-Ferrous Structural Sheet Materials at Elevated Temperatures. Part V.'
Wright Air Development Center, A.F. Tech. Report 6517, Dec. 1957; 90 pp. *P.B.* 131595.

The tensile and compressive extensometers used in previous investigations by the present author were found to be inherently unsuitable for tests at temperatures higher than 600°F. (315°C.). Supplementary tests, using an extensometer designed specifically for high-temperature work, were therefore carried out to obtain more accurate values for tensile and compressive moduli of elasticity, and to gain data on the bearing strength of the materials for an edge-distance ratio of two.

The materials tested comprised aluminium alloys, magnesium alloys, titanium, low-alloy chromium-molybdenum steel and two types of 18–8 chromium-nickel stainless steel (A.I.S.I. 301 and 302).

Previous data had indicated that time of exposure had no consistent or significant effect on the moduli of elasticity: temperature was therefore the only test condition which was varied. The test materials had, however, been in storage for periods ranging from 3–5 years and the effects of this protracted room-temperature ageing were also taken into account in assessing the results. The specimens were held at the test temperature for 30 minutes prior to testing.

The stainless steels (Type 301 in the half-hard, and Type 302 in the annealed condition) were tested at 400°, 600°, 800° and 1000°F. (205°, 315°, 425° and 535°C.). Tensile tests were not made on these two materials.

Analysis of the data obtained, which are presented in tabular and graphical form, indicated that, in general, the strength properties and moduli of elasticity of the materials decrease with rise in temperature. The elevated-temperature properties of fully-annealed materials, in contrast to those which had been hard-rolled, appeared to be unaffected by long storage at room temperature. The values for the Type 302 stainless steel (which had been annealed) were found to be similar to those determined in the previous investigation. The half-hard Type 301 steel, however, exhibited greatly improved compressive yield strength: superior, at all temperatures, to the tensile yield strength determined in the original tests. It is suggested that this effect might be attributable partly to stress relief resulting from the long period of storage.

Oil-Ash Corrosion: Review of Present Knowledge

N.A.C.E. TECHNICAL COMMITTEE: 'The Present Status of the Oil-Ash Corrosion Problem.'

N.A.C.E. Publn. 58-11.
Corrosion, 1958, vol. 14, Aug., pp. 369t-72t.

The paper represents the first report of the National Association of Corrosion Engineers Task Group assigned to study the problem of oil-ash corrosion. Five case histories of typical oil-ash-corrosion failures are described, as a means of emphasizing the characteristic features of this type of attack, and an outline is given of the measures which have been suggested to combat the problem. The relative success of each of these approaches is discussed, and the directions in which work in this connexion is likely to be most fruitful are considered.

The case histories relate to failures in 'Inconel' and 25-20 and 25-12 chromium-nickel-steel components used in oil-fired furnaces, heaters and superheater units.

Means of preventing or minimizing oil-ash corrosion have been sought along five main lines. An appraisal is given of the problems each entails.

Treatment of the oil before use, to remove the vanadium, sodium and sulphur compounds to which oil-ash corrosion is attributed, is costly and would have to take into account variations in the compositions of oil from different sources. Reference is, however, made to a procedure in current use for reducing the sodium-salt content of residual oil.

Protective coatings applied to components exposed to oil-ash corrosion would have to withstand the effects of thermal cycling and high temperatures, in addition to exhibiting satisfactory corrosion-resistance. 'Duralized' specimens have shown some promise, but at present this approach to the problem has not met with great success.

Work on additives to inhibit corrosion has related mainly to compounds of magnesium, calcium, zinc, phosphorus and aluminium, and, after listing the characteristics required of an additive for effective inhibition, the report briefly summarizes the results obtained with such compounds.

The development of suitably resistant materials is a problem which is aggravated by the wide variation in corrosive conditions represented by the term 'oil-ash corrosion'. The report refers, for example, to the fact that at temperatures up to 815°C. high-nickel alloys such as 'Inconel' and 'Inconel X' are resistant to attack by vanadium pentoxide alone, and that, except under reducing conditions, sodium sulphate is not highly corrosive to the austenitic steels. In practice, however, mixtures of the two corrosives (the most deleterious contains about 15 per cent. Na_2SO_4 and 85 per cent. V_2O_5) are encountered, and the effects are more than additive. Although chromium-nickel stainless steels and alloys such as 'Inconel' are satisfactory for use under normal high-temperature conditions, no alloy so far developed has offered high resistance to oil-ash corrosion in the range 1600°-1800°F. (870°-980°C.).

With respect to *changes in design*, the report mentions the desirability of lowering operating temperatures to below 1200°F. (650°C.), and refers briefly to the influence, on oil-ash corrosion, of the air/fuel ratio.

It is considered that the most promising lines of approach to the problem are in development of suitable inhibitors; treatment of the oil to lower the sodium and vanadium contents; development of alloys with suitably resistant surface oxide films; investigation of aluminized and siliconized coatings; study of the fundamental mechanisms involved in the corrosion.

Machining of Stainless-Steel Gas-Turbine Blades

'Machining Blades for Gas Turbine Units: Methods Employed by B.R.D. Co., Ltd., Aldridge, Staffs.'

Machinery (*Lond.*), 1958, vol. 93, Aug. 20, pp. 400-11.

The article, which is one of a series describing the methods and machinery employed by the B.R.D. Company, Ltd,, in the production of blades for gas-turbine units, outlines the operations involved in machining stainless-steel compressor blades used in the 'Proteus' turbo-prop engine of Bristol Aero Engines, Limited.

The blades are received in the form of slightly oversize forgings. The initial operations are concerned with the machining of the location surfaces which provide a means of positioning the workpiece during subsequent machining. A series of milling operations is then carried out on the root portion of the blade, and the aerofoil surfaces are machined to the required shape. Finally the blades are hand-finished and cut to the required overall length.

The sequence of operations is followed through in detail and descriptions of the machinery are supplemented by annotated photographs.

Glossary of Terms Used in Reference to Corrosion

'Inter-Society Corrosion Committee Glossary of Corrosion Terms, Part II.'
N.A.C.E. Publn. 58-9.

Corrosion, 1958, vol. 14, July, pp. 319t-20t.

The glossary, submitted by the N.A.C.E. Sub-Committee on Standard Definitions and Terminology at the 1958 meeting of the Society, contains definitions of fifty terms. For the first list, see *N.A.C.E. Publn.* 58-5 (*ibid.*, 1958, vol. 14, Feb., pp. 71t-2t).

Corrosion-Resistance of Precipitation-Hardenable Stainless Steels

J. HALBIG and O. B. ELLIS: 'Observations on Corrosion Resistance of High-Strength Stainless Steels for Aircraft.'

Corrosion, 1958, vol. 14, Aug., pp. 389t-95t.

Stainless steels of the semi-austenitic precipitation-hardenable type are finding increasing application as materials of construction for airframe components in high-speed aircraft: they offer not only the desired property of high strength (conferred by martensitic transformation) but also the advantages inherent in their 'stainlessness' and ease of fabrication. Corrosion-resistance is one of the combination of properties which the authors lay down as essential to an ideal air-frame material. During the last decade considerable data have been assembled on the corrosion-resistance of the '17-4 PH', '17-7 PH' and 'PH 15-7Mo' precipitation-hardenable steels produced by the Armco Steel Corporation: in this paper the authors summarize information culled from the literature and unpublished reports. For purposes of comparison, corrosion data are included also on the straight-chromium grades of stainless steel. The nominal compositions of the three precipitation-hardenable steels are given in table 1 below.

The review is introduced by a short résumé of the forms in which the steels are available and of the heat-treatments represented by the designations 'A', 'T', 'C' and 'H'. (The heat-treatments and designations for '17-7 PH' and '17-4 PH', and the mechanical properties achieved in each condition, are summarized in tabular form in *Nickel Bulletin*, 1958, vol. 31, No. 2, p. 52; heat-treatment for the 'PH 15-7 Mo' steel is similar to that for the '17-7 PH' grade. Other abstracts relating to the compressive and tensile properties of such steels will be found in *Nickel Bulletin*, 1958, vol. 31, No. 1, p. 16; No. 3, p. 81.)

Achievement of optimum corrosion-resistance in the steels is stated to be dependent on observance of the following precautions: thorough cleaning before heat-treatment; removal of scale or oxide films by mechanical methods rather than by pickling; correct control of furnace atmospheres during heat-treatment; selection of the most suitable heat-treatment. Accelerated corrosion tests showed that nitriding reduced the corrosion-resistance of the steels.

The authors' review of the corrosion-resistance of the three steels is presented in sections relating to their behaviour when exposed to the particular corrosive media indicated below.

General Corrosion Data

Tabular data are presented, derived from an extensive programme of accelerated-corrosion tests involving exposure to various concentrations of sulphuric acid, hydrochloric acid, nitric acid, formic acid, acetic acid, phosphoric acid and sodium hydroxide. Comparative data are included on a straight-chromium and an 18-8-type chromium-nickel stainless steel. The data indicate that the corrosion-resistance of the precipitation-hardenable steels is higher than that of the chromium steel, but (with the exception of the '17-7 PH' grade which exhibits similar resistance to many of the media investigated) lower than that of the '18-8' grade.

Fuming Nitric Acid

Discussion in connexion with resistance to fuming nitric acid relates only to the '17-7 PH' steel. Corrosion in both white and red fuming nitric acid appears to be temperature-dependent, but in the TH 1070 condition the resistance of the steel to red fuming nitric acid is satisfactory, provided that the acid is inhibited by suitable addition of hydrofluoric acid.

High-Temperature High-Purity Water

References are made to literature which indicates that the '17-4 PH' and '17-7 PH' steels have excellent resistance to corrosion, at high temperatures, by high-purity water. The materials are, however, subject to stress-corrosion cracking; correct ageing will ensure immunity to this type of failure.

Table I

Compositions of Precipitation-Hardenable Stainless Steels

Steel	C %	Cr %	Ni %	Mo %	Al %	Cu %	Nb-Ta %
'17-4 PH'	0·04	16·20	4·00	—	—	3·50	0·25
'17-7 PH'	0·07	17·00	7·00	—	1·15	—	—
'PH 15-7 Mo'	0·07	15·00	7·00	2·25	1·15	—	—

Sea Water

Some data (on '17-4 PH', '17-7 PH', two chromium and two chromium-nickel stainless steels) are given in connexion with tests involving long-time exposure to sea water. The corrosion rates for all the steels were low (≯3 mils per year) and are, in this respect, misleading, since loss in weight was due almost entirely to crevice corrosion. However, in applications where formation of deposits and presence of crevices are not a problem '17-4 PH' has given satisfactory service.

Marine and Industrial Atmospheres

Specimens of the three precipitation-hardenable steels, a straight-chromium and an '18-8' type stainless steel were exposed at locations representative of marine and mild industrial atmospheres. The results are discussed in this section; photographs illustrating the appearance of the specimens after exposure to these atmospheres are also presented. The corrosion-resistance of the hardenable steels varied with the heat-treatment to which they had been subjected, but that of the precipitation-hardenable grade was in all cases superior to the resistance of the straight-chromium types. Changes in the mechanical properties of the steels were correlated with relative corrosion-resistance as assessed by appearance. Assessment by the two criteria gave consistent results. The data are regarded as indicative of the excellent resistance of the three steels to atmospheric conditions.

Galvanic Corrosion

Cases of galvanic corrosion involving the hardenable stainless steels are, in the authors' experience, extremely rare.

Stress-Corrosion Cracking

Failure by stress corrosion is discussed mainly in relation to the results published by BLOOM (see *Nickel Bulletin*, 1955, vol. 28, No. 11, pp. 198-9).

The paper ends with brief mention of a 92·5/7/0·5 silver-copper-lithium brazing alloy reported to be resistant to crevice corrosion, and of the satisfactory resistance to atmospheric corrosion of inert-gas arc-welded '17-7 PH' sheet.

Corrosion by Fuming Nitric Acid: Inhibition by Hydrofluoric Acid

D. M. MASON and J. B. RITTENHOUSE: 'Mechanism of Inhibiting Effect of Hydrofluoric Acid in Fuming Nitric Acid on Liquid-Phase Corrosion of Aluminium and Steel Alloys.'

Corrosion, 1958, vol. 14, July, pp. 345t-7t.

Previous investigations by the authors had shown that with aluminium alloys and certain steels, corrosion by fuming nitric acid, in both the liquid and gas phases, was inhibited by the presence of 0·2-1·0 wt. per cent. of hydrofluoric acid (see abstracts in *Nickel Bulletin*, 1957, vol. 30, No. 4, p. 62; No. 7-8, p. 141; *ibid.*, 1958, vol. 31, No. 3, pp. 90-1). Their findings had indicated that inhibition was due to a passivating process resulting from formation, on the surface of the metal, of a tenacious insoluble metallic fluoride. This paper presents the results of a supplementary investigation which was carried out in an attempt to corroborate this explanation of the mechanism of hydrofluoric-acid inhibition. (A subsidiary aim of the investigation was to determine whether the entire solution needed to be saturated for effective passivation over a storage period of several months.)

The proposed mechanism was examined in relation to corrosion, in inhibited thermally-stable nitric acid (containing 14 wt. per cent. of NO_2 and 3 wt. per cent. of H_2O), of the following materials: an aluminium alloy, 1 per cent. chromium steel, and 13 per cent. chromium (A.I.S.I. Type 410) and 18-8 (Type 347) chromium-nickel stainless steel. The investigation comprised three stages: (1) measurement, as a function of temperature, of the solubility in fuming nitric acid of aluminium nitrate, and of the fluorides of aluminium, iron, chromium and nickel; (2) correlation of the solubility data with the corrosion rate, in inhibited fuming nitric acid, of the alloy or steel to which the fluoride pertained; and (3) analysis of the passive film formed on the materials investigated.

The data obtained are regarded by the authors as further substantiation of the proposed mechanism. That effective passivation depends on saturation by the fluoride was established by correlation of the corrosion data before saturation with solubility data for the relevant fluoride (as shown, for example, in the similarity of the two curves obtained for the chromium-nickel stainless steel). The main constituent of the passive film formed on the steels was found to be an iron fluoride admixed with FeO or Fe_3O_4; that on the 18-8 steel also contained 20 per cent. chromium and 8 per cent. nickel. That chromium and nickel fluorides play a rôle in the passivation process was indicated by the fact that passivation was facilitated by increase in alloy content. Saturation of the fuming-nitric-acid solution with compounds which comprise the passive film on this stainless steel reduced the degree of corrosion required to achieve passivation.

The results of uni-dimensional diffusion studies, involving measurement of the concentration of metal-ion products of corrosion as a function of time and distance from the metal, gave further support for the solubility mechanism of inhibition.

Behaviour of Steels in Hydrogen-Sulphide Environments

L. W. VOLLMER: 'The Behaviour of Steels in Hydrogen-Sulfide Environments.'

Corrosion, 1958, vol. 14, July, pp. 324t-8t.

The failure of steels exposed under stress to hydrogen-sulphide environments (conditions which, for example, obtain in the production of sour heavy crude oil from deep high-pressure condensate wells) has been

the subject of intensive research. Literature relating to 'sulphide stress cracking' (a term which the author considers more accurate than the commonly used 'sulphide corrosion cracking') is voluminous: he therefore makes no attempt at a comprehensive review of the subject, but limits his paper to discussion of the following aspects: (1) mechanisms advanced to explain sulphide stress cracking of steels; (2) apparatus and techniques used to establish susceptibility to such failure; (3) general conclusions which may be drawn from past work with respect to metallurgical and environmental conditions which contribute to its occurrence; (4) precautions which, in the light of these conclusions, might be expected to minimize susceptibility to sulphide stress cracking. The data relate mainly to 'N-80' (manganese-molybdenum) tubing steel which is commonly used in wells producing sour condensate fluids.

The theory that absorption of nascent hydrogen by the steel under stress is a major contributory factor in sulphide stress cracking forms the basis for discussion of possible causes and mechanisms. In his review of techniques for testing susceptibility to cracking, the author describes the use of U-bend beam and tensile specimens.

Much of the work carried out on sulphide stress cracking has been in relation to the significance of microstructure and critical stresses. Findings of importance are summarized and reference is made in this connexion to the influence of composition, the presence of martensite, the critical stress above which a susceptible steel will fail, and the effects of plastic deformation and of charging the steel, under stress, with hydrogen.

Finally, the author outlines measures which appear likely to minimize susceptibility to cracking. These precautions include the elimination, by heat-treatment, of martensite or other deleterious phases, and limitation of the yield strength of the steel, to ensure an adequate margin of safety. Stresses in the equipment should be minimized as far as possible, and haphazard cold-deformation and use of welded joints should be avoided. Where the application of high-strength materials is essential, use is recommended of alloys which have high resistance to sulphide stress cracking (e.g. 'K Monel', 'Inconel' and those of the 'Hastelloy' series). If the use of high-strength steels is unavoidable, resistance to cracking can be conferred by deposition of a ductile non-porous nickel coating.

Intercrystalline Corrosion of Stainless Steel in Alkaline Solutions

J. N. WANKLYN and D. JONES: 'The Intercrystalline Corrosion of Stainless Steel in Alkaline Solutions.' *Chemistry and Industry*, 1958, No. 28, July 12, pp. 888-9.

It is known that exposure to sodium-hydroxide solutions, or to steam contaminated with the caustic can cause stress-corrosion cracking in austenitic chromium-nickel steels (see, for example, WILLIAMS, *Corrosion*, 1957, vol. 13, Aug., pp. 539t-45t; *Nickel Bulletin*, 1957, vol. 30, No. 11, p.208-9). Such cracking like that due to the presence of chlorides, is reported to be transcrystalline. During experiments in connexion with the corrosion of materials under heat-transfer conditions, in water similar to that used in the primary circuits of pressurized-water nuclear reactors, the authors discovered that cracking in water contaminated with potassium hydroxide (which is added to raise the pH to a value of 10-11) was entirely intercrystalline. The results of the experiments are presented in this brief report.

It seemed likely that the heat-transfer conditions, which involved boiling at the metal surface, would produce a sufficient concentration of alkali to cause stress corrosion of austenitic stainless steels. Dynamic corrosion tests were therefore carried out, in potassium - hydroxide - contaminated water (pH 11, temperature 280°C.), on strips of niobium- and titanium-stabilized 18-8-type chromium-nickel stainless steels which were electrically heated, to produce boiling heat-transfer conditions, and subjected to a stress of about 20,000 p.s.i. (9 t.s.i.; 14 kg./mm.^{2}).

Stress corrosion was induced only when the stainless-steel strips were arranged face to face to form a deep crevice; under these conditions, however, the specimens consistently cracked within an exposure time of 100-200 hours, and, in every case, the cracking was entirely intercrystalline. The outer faces of the strips were unaffected. When the pH of the water was reduced to 7 no sign of incipient cracking was found in the niobium-stabilized grade after exposure for 280 hours.

Two possible causes of the cracking were investigated. Local rise in temperature, at the base of pits or incipient cracks, due to 'bunching' of the electric current used to heat the strips, was ruled out as a contributory factor, since such temperature variations were found to be negligible. The second factor, that of the concentration of alkali within the crevice (estimated at 50 wt. per cent.), was studied in corrosion tests on titanium-stabilized stainless-steel tube specimens, which were filled with aqueous solutions containing 10, 25, or 50 per cent. of potassium hydroxide, and then heated to achieve steam pressures of between 10,000 and 20,000 p.s.i. All the tubes failed within 200 hours. They exhibited a combination of trans- and intercrystalline cracking, the latter type predominating, and it is therefore concluded that concentrated solutions of caustic alkali can cause intercrystalline as well as transcrystalline cracking of austenitic steels. The precise conditions of concentration, temperature and stress to produce each type of cracking have yet to be determined.

Resistance of 'Monel' and Stainless Steel to Corrosion by Sea Water

C. V. BROUILLETTE: 'Corrosion Rates in Port Hueneme Harbor.'

Corrosion, 1958, vol. 14, Aug., pp. 352t-6t.

To determine the general corrosion behaviour of various structural materials when exposed to

the harbour sea water of Port Hueneme, California, 16 metals, alloys and steels were totally immersed in the water for periods ranging from 6 to 30 months. The materials investigated consisted of copper; lead; aluminium- and magnesium-base alloys; aluminium, phosphor and manganese bronzes; naval brass; 'Monel'; low-carbon steel; and 18–8 type chromium–nickel stainless steel. Corrosion rates for each material were determined, and are presented, as mils per year and mg./dm.^{2} per day. Pitting contributed appreciably to the corrosion rates of some of the specimens and data on the depths of pits are also included.

The corrosion behaviour of each material is discussed. The magnesium-alloy specimens were found to be the most readily attacked, while lead exhibited the greatest corrosion-resistance. Corrosion on aluminium specimens occurred mainly in the form of pitting. The 'Monel' and stainless steel also exhibited this type of attack: in the case of 'Monel', pitting was accelerated by the presence of marine organisms, but except for the pits, the surface remained smooth and apparently free from attack; pitting of the stainless steel was typical of that previously reported for specimens immersed in slow-moving or stagnant sea water. The copper, brasses and bronzes corroded only slightly, with no signs of pitting. The carbon steel was rapidly corroded.

Water Wettability of Stainless-Steel Surfaces

See abstract on p. 289.

Stainless Steel in Uranium-Refining Plant

F. W. FINK, W. J. BRAUN and D. M. STEWART: 'The Corrosion of Type 347 Stainless Steel in Boiling Digest Liquors.'

Battelle Memorial Inst. Report 1252, Jan. 28, 1958; 26 pp. + appendix.

At the Mallinckrodt Uranium Refining Center uranium concentrates are digested, at an early step in the process, in a nitric-acid solution. The resultant solution is known as digest liquor. Many other elements, as well as uranium, are dissolved from the feed material.

Austenitic stainless steel (A.I.S.I. Type 347) is at present used for the vessels in which this stage of the process is carried out, and it has been observed that pitting and local attack occurs on welded joints. It was suspected that the corrosiveness of the digest liquors might vary with variations in the nature and content of the contaminants in the feed materials and with the amount of free nitric acid present in the liquor. There was also the possibility that uranium raw materials from newer sources, currently being refined, might give rise to digest liquors much more corrosive than any which had been previously processed.

This report describes an experimental evaluation of the effects of variations in the composition of the feed and in the concentration of free nitric acid, on stainless steels, also with methods for controlling attack.

The results indicate that the digest liquors now used should not be excessively corrosive to the chromium–nickel stainless steel, but that liquors resulting from some of the newer sources of uranium concentrates could become corrosive if the fluoride, chloride or free-nitric-acid contents are at abnormal levels.

It was demonstrated that, in liquors containing relatively high concentrations of fluoride, additions of aluminium will reduce the attack, in both liquid and vapour phases. Additions of iron may be used in inhibiting corrosion arising from high levels of chlorides. An extra-low-carbon 18–8 type of steel appears to possess corrosion-resistance comparable with that of the Type 347 steel and that of the more complex 'Carpenter No. 20' type (containing copper and molybdenum in addition to high percentages of chromium and nickel). 'Haynes Alloy No. 25' (cobalt-base alloy containing chromium, nickel and tungsten) showed a somewhat lower rate of corrosion penetration, but there was a tendency to formation of a loose insoluble corrosion product, which might be objectionable in service.

High-Nickel Alloys in Butane-Isomerization Units

J. F. MASON and C. M. SCHILLMOLLER: 'What To Do About Corroding Isomerization Units.'

Petroleum Refiner, 1958, vol. 37, July, pp. 103–6.

The information given in the article is intended to serve as a guide to engineers and designers concerned with the planning and/or operation of butane-isomerization units. The review is essentially practical: corrosion problems associated with such plants are discussed in the light of operational experience, with notes on measures adopted to prevent corrosion.

Because of the nature of the catalyst and the recycling of anhydrous hydrochloric acid, corrosion in isomerization units is related directly to the formation of aqueous hydrochloric acid and to the presence, in the system, of sludges which absorb chlorides. Resistance to attack by hydrochloric acid is therefore a prerequisite for the material of construction. Nickel and high-nickel alloys are among the few metallic materials which exhibit satisfactory resistance to these conditions, and, by way of introduction to case histories (discussion of which forms the major part of the article), the authors present corrosion data for nickel, and for wrought and cast alloys of nickel–molybdenum–iron, nickel–silicon and nickel–copper base.

The case histories are considered in relation to the two processes used in isomerization of butane (vapour-phase and liquid-phase). The authors indicate the stages in each process in which conditions are particularly conducive to corrosion, and emphasize, by reference to the case histories, the need for process control and the use of appropriate materials of

construction (preferably high-nickel alloys). The feed should be dry (water content not exceeding 10 p.p.m.) and should contain a minimum of impurities such as sulphur, pentanes and olefins. Where, despite such precautions, corrosion is still a problem, the solution must be sought in the use of corrosion-resisting materials for the plant. Nickel-clad steel has, for example, been used to withstand the highly corrosive conditions which prevail in the reactors: satisfactory service of more than five years has been obtained.

Use of 'Monel' in Mercaptan-Extraction Plant

C. H. BAND and A. CLUER: 'Application of the 'Unisol' Process in Great Britain.'

Petroleum, 1958, vol. 21, Sept., pp. 305–8.

The thermal-cracking unit used at the Ellesmere Port Refinery of Lobitos Oil Fields, Ltd., was installed in 1940. At that time the plant processed only low-sulphur residues, from Peruvian and Ecuadorian crude oils; it was therefore designed on the assumption that, since no significant quantity of straight-run gasoline would be present in the feed-stock, no provision need be made for segregating straight-run gasoline from the cracked product. In 1950, however, it became necessary to use sour crude oil from Kuwait as feed to the pre-topping/cracking plant, and the engineers were confronted with the problem of sweetening the straight-run and cracked gasolines which would be produced. The straight-run type presented no difficulty, since its mercaptan content was similar to that of the Peruvian gasolines, but the cracked gasoline, which was expected to have a mercaptan sulphur content of approximately 0·06 to 0·09 wt. per cent. (i.e., about ten times as sour as anything previously handled) would not, without special treatment, meet the relevant specifications. Extraction of the mercaptans was, therefore, essential. This article describes the 'Unisol' extraction process (licensed by Universal Oil Products Company) which was selected as the most suitable of the methods considered.

An outline (with flow diagram) is given of the plant involved and of the various stages of the process; the problems encountered are discussed, and typical results are quoted. The section giving details of materials used in the plant is concerned mainly with 'Monel'. Conventional materials are used in all sections with the exception of that handling hot caustic: in the caustic-regeneration section, where corrosion and embrittlement were expected, 'Monel' has been used for various parts, amongst which are the caustic stripping column, the re-boiler, pipe work, hot regenerated-caustic lines and part of the regenerated-caustic/spent-reagent heat exchanger. All valves in that section are in 'Monel' or nickel. The advantage of using 'Monel' for such applications was emphasized by experience in the early operation of the plant, when, because 'Monel' was not available, lines handling caustic were made from mild steel. The steel pipes corroded within a few months, whereas 'Monel' lines showed little corrosion after four years' operation.

Nickel-containing Materials in Plant Producing Phosphoric Acid

J. C. BARBER: 'Corrosion Problems in the Manufacture of Phosphoric Acid from Elemental Phosphorus.'

Corrosion, 1958, vol. 14, Aug., pp. 357t–62t.

Phosphoric acid is manufactured on a commercial scale by two processes: the wet and the electric-furnace process. In the latter process elemental phosphorus, produced in an electric furnace from phosphate ore, coke and silicon, is burnt in air to form P_2O_5, which is then reacted with water to produce H_3PO_4. The acid normally contains 55 to 60 per cent. of P_2O_5. Phosphoric acid is *per se* a highly reactive chemical, and the corrosion problems involved in its manufacture are further intensified by the very high temperatures which are a necessary feature of the electric-furnace technique. Corrosion data with respect to phosphoric acid have been derived mainly under closely controlled laboratory conditions, and their relevance to actual service conditions is uncertain. This paper is intended to supplement such information with corrosion data derived from tests carried out in a plant producing the acid from elemental phosphorus.

The paper is in two sections. The first describes the sequence of the process and the plant used at each stage: i.e., combustion of the phosphorus (in the vaporizer and the burner); hydration of the P_2O_5 and collection of the acid (in the hydrator); recovery of the acid mist and exhaustion of waste gases (by means of the Venturi scrubber and the exhaust fan). In the second part of the paper the corrosion problems encountered in different parts of the plant are outlined, and the suitability of various materials for applications involving corrosive conditions is discussed.

In the vaporizer, burner, and hydrator corrosion during combustion has been minimized by the use of refractory linings such as water-cooled graphite blocks.

The Venturi scrubber is subjected both to corrosion and to erosion by acid particles in the gas stream. The results of laboratory tests to determine the effect of temperature on the corrosion rates of 18–8 (Type 316) chromium-nickel-molybdenum steel (the stainless steel used in the fabrication of the scrubber) are presented. The steel was found to be satisfactorily resistant to attack at temperatures up to 225°F. (105°C.). Corrosion rates derived from other tests, in which Type 316 steel was exposed in various parts of the scrubber, ranged from 12 to 217 mils per year. The cone section of the Venturi scrubber, which is exposed to gas travelling at a velocity of 120 ft. (36 m.) per second, corroded at a rate of 93 mils per year. Further corrosion tests were made in an attempt to find materials which would prove more resistant than the 18–8-type stainless steel in this application: data on relevant performance are tabulated for 'Ni-O-Nel' (a nickel-chromium-iron alloy), 'FA 20' (a nickel-chromium-copper-molybdenum alloy), the nickel-containing alloys

'Chlorimet 3', 'Hastelloy B' and 'Monel', and the following stainless steels: 'V 2B', 'Durimet 20', A.I.S.I. Types 201 (chromium-manganese-nickel) and 430 (a straight-chromium grade), and '17-4 PH'. 'Ni-O-Nel', 'V 2B' and 'FA 20' were slightly more resistant than Type 316 stainless steel. The chromium-manganese-nickel steel exhibited slightly inferior resistance to corrosion.

The Type 316 stainless-steel impeller of the fan used to exhaust the waste gases failed, as a result of weld decay, after only two months' service; substitution of the extra-low-carbon grade of the steel (Type 316 L) effectively solved this problem. To determine the most suitable material for the duct through which the exhaust gases were led to the stack, corrosion tests were carried out on nickel, copper, various chromium and chromium-nickel stainless steels, 'Hastelloy B', various grades of 'Monel', 'Inconel', 'Ni-Resist', mild steel, cast iron, and 'Carpenter 20' stainless steel. Of these materials, only 'Type 316' stainless steel, 'Carpenter 20', nickel and 'Hastelloy B' had corrosion rates of less than 50 mils per year. Welded specimens of the Type 316 stainless steel exhibited corrosion-resistance similar to that of unwelded specimens, and ducts fabricated from this material have given satisfactory service for more than five years.

Use of 'Monel' in Salt-Water Cooling Towers

W. W. MITCHELL: 'Short of Fresh Water? Use Salt-Water Cooling Towers.'

Chemical Engineering, 1958, vol. 65, June 16, pp. 181–2.

In planning the expansion of their oil refinery at Perth Amboy, New Jersey, the California Oil Company were faced with the problem of providing sufficient cooling water for the refinery's catalytic re-former. Sources of fresh water within reasonable distance of the refinery were limited and, in 1956, a salt-water cooling tower was erected which was eventually to have a capacity of 15,000 g.p.m. Treatment of the salt water was found to be unnecessary. Further expansion has resulted in a demand for a new supply of cooling water, and a second cooling tower, capable of handling 12,000 g.p.m., is now in the planning stage. The two salt-water cooling towers will, it is believed, be the only ones in service in the chemical-refinery industry. This article, which includes a flow sheet, describes the salient features of the design of the new tower and briefly discusses the materials used for the main components.

Operational experience gained with the first tower has led to extensive use of 'Monel' as a material of construction in the second. Stainless-steel cases and impellers are specified for all the pumps. The shafts of the pumps, the fan blades and laminated disc assemblies of the drive coupling are to be in 'Monel', and the same alloy is to be used for all anchor bolts, screens and other components immersed in the cooling-tower basin.

Use of Stainless Steel for Tug Boats and Diesel Railcars

'New Inland-Waterway Towboats have Welded Stainless-Steel Hulls.'

Welding Jnl., 1958, vol. 37, Aug., p. 805.

The three twin-screw inland-waterway tug boats, the 'U.S.S.1', 'H.B. Jordan' and 'S.N. Jenks', are unique in that they are the first to be built with stainless-steel hulls. These vessels, in which stainless steel was specified for all parts exposed to water (including rudders, shafting and propellers), were built by St. Louis Shipbuilding and Steel Company: they ply on the Ohio and the Monongahela Rivers. About 18 tons (18,288 kg.) of $\frac{3}{8}$-, $\frac{5}{16}$-, and $\frac{1}{4}$-in. (9-, 8-, and 6-mm.) stainless-steel plate were used in the fabrication of the first boat, and about 40 tons (40,640 kg.) of plate and 8 tons (8,128 kg.) of stainless-steel forgings and castings in each of the others. Their construction entailed deposition of approximately 10,500 ft. (3,150 m.) of welds, and use of $1\frac{1}{2}$ tons (1,524 kg.) of electrodes. The details are contained in a brief note which is supplemented by photographs of the ships.

'Australian-built Railcars for Malayan Railway.'
Railway Gazette, 1958, vol. 109, Sept. 12, pp. 307–8.

The article describes the salient features of a 500-h.p. diesel-hydraulic railcar designed by Commonwealth Engineering Company, Ltd. Six of these cars are now being delivered to the Malayan Railway. Notes are given on the construction of the car, its engines, control, engine cooling, compressors, bogies and electrical equipment.

The car is constructed (by the 'Budd Shotweld' process) from stainless steel, the slightly higher cost of which is expected to be counterbalanced by savings in maintenance costs.

Diffusion Bonding of 'Monel' to Copper-Beryllium Alloy

J. T. NIEMANN, R. P. SOPHER and P. J. RIEPPEL: 'Diffusion Bonding Below 1000°F.'

Welding Jnl., 1958, vol. 37, Aug., pp. 337S–42S.

The paper describes investigations involved in development of a diffusion-bonding technique suitable for joining a copper-beryllium alloy (containing 2 per cent. beryllium) to 'Monel'. More specifically, the requirement was for joining the two components of water-cooled throat blocks used in hypersonic wind tunnels, viz., the contoured 'Monel' backing block to the copper-beryllium cover sheet. The block and its two components are illustrated. The cover sheet was to be joined to the block along all the edges and interior ribs so as to seal the water-cooling passages and provide sufficient strength to withstand an internal pressure of 1500 p.s.i. (1 kg./mm.^{2}); the plate itself was to have a minimum tensile strength of 180,000 p.s.i. (80 t.s.i.; 126·5 kg./mm.^{2}), which was to be achieved by solution annealing at 1400°F. (760°C.), water quenching, and

finally ageing for three hours at 650°F. (345°C.). If brazing were used it would have to be effected at a temperature above that of solution annealing, and would therefore necessitate quenching from 1400°F. (760°C.), a process which was found to result in distortion of the 'Monel' block. Diffusion bonding of the two components would, however, obviate the need for quenching the composite (since the copper-beryllium sheet could be bonded in the annealed condition), and if the bonding was carried out for three hours at 650°F. (345°C.), it would simultaneously achieve the ageing necessary to attain the desired tensile strength.

Previous experience had shown that it was difficult to obtain satisfactory diffusion-bonded joints between the two alloys. One inhibiting factor was the oxide film which forms on the surface of the copper-beryllium, and it was therefore decided to investigate the possibly beneficial effect of electroplating each component with one or other of two metals which, at the bonding temperature, would exhibit a greater tendency to diffuse. The combinations tested, the suitability of which is assessed on the basis of their tendency to form solid solutions or intermetallic compounds, were: silver with copper; gold with silver, lead, copper, aluminium or nickel; and nickel with silver or iron. Satisfactory bonding was obtained with the gold/copper, gold/silver, gold/lead and gold/aluminium combinations. (Photomicrographs of some of the bonds are given.)

Further experiments were carried out, with the gold/copper combination, to determine the variation of the depth of the diffusion zone with time and temperature. Temperature was found to have the greater influence, and it was concluded that no advantage would be gained, in relation to the bonding conditions, by changing the time or temperature of the age-hardening treatment.

To determine the combination of electrodeposits which would achieve the strongest joints, a study was made of the shear strengths of diffusion bonds obtained with the four systems previously mentioned. The gold/copper and gold/silver combinations were deemed to have sufficient tensile strength, at least 20,000 p.s.i. (9 t.s.i.; 14 kg./mm.^{2}), for use in the throat block: the gold/lead and gold/aluminium joints were very brittle. Further tests were made, using the gold/copper system, on simulated throat blocks, to establish the optimum thickness of the copper-beryllium-alloy sheet, i.e., the thickness at which, under hydrostatic loading for three hours at 650°F. (345°C.), the sheet would be thin enough to conform to the contour of the block without being depressed into its channels. Diffusion-welding sheet 0·090-in. (2-mm.) thick to 'Monel', in a helium atmosphere and under a hydrostatic pressure of 1500 p.s.i. (1 kg./mm.^{2}), produced joints which successfully withstood an internal pressure of 6500 p.s.i. (3; 4·5 kg./mm.^{2}). The paper gives details of the specimens and procedure used.

Tungsten-Arc Cutting Process

See abstract on p. 289.

Porosity in High-Nickel-Alloy Welds: Causes and Control

G. R. PEASE, R. E. BRIEN and P. E. LEGRAND: 'The Control of Porosity in High-Nickel-Alloy Welds.' *Welding Jnl.*, 1958, vol. 37, Aug., pp. 354S-60S.

Porosity in weld deposits has been attributed to the ejection, at the solidus, of gases previously taken into solution by the molten weld metal. Identification of those gases which are deleterious in this respect, and determination of the behaviour of the specific weld material in which they are present, are therefore of importance. Such investigations have been carried out on some materials (hydrogen, nitrogen and oxygen are reported, for example, as possible sources of porosity in mild-steel welds) but little work has been done on the high-nickel alloys. The investigation described in the paper contributes towards filling this gap.

The generic term 'high-nickel alloys' was extended by the authors to include not only the nickel-copper alloys 'Monel' and the nickel-chromium-iron alloy 'Inconel', but also a commercial grade of nickel. These three materials were selected as typical of those of nickel base, findings for which would probably be applicable also to other nickel alloys. Comparative data were obtained for mild steel and several grades of 18-8-type chromium-nickel stainless steels.

The influence of five gases was studied: hydrogen, oxygen, nitrogen, carbon monoxide and carbon dioxide. In general, the weld metal was deposited, without filler metal, by the inert-gas-shielded tungsten-arc process, and the contaminant gas was introduced, *viâ* the helium shielding gas, in amounts intended to produce concentrations of up to 10 vol. per cent. at the nozzle of the torch. Contamination by carbon dioxide was effected using the inert-gas-shielded consumable-electrode technique and filler wire; hydrogen was introduced by means of a welding torch in which the gas is normally employed as a shroud. The degree of porosity in each weld was assessed on the basis of the number of gas holes per linear inch of weld bead. Welding conditions are recorded.

The relative porosity resulting from contamination by each of the five gases is illustrated in graphical form. For results and conclusions see below.

Of the gases studied, nitrogen was found to have the most deleterious effect on the soundness of the weld deposits. As little as 0·1-0·2 per cent. was sufficient to induce traces of porosity in 'Monel' and nickel, and at 1 per cent. the gas caused very severe porosity. Nitrogen in amounts up to as much as 10 per cent. had no effect either on the stainless steels or on 'Inconel'.

It is concluded also that (1) avoidance of contamination by nitrogen is essential if sound welds are to be achieved in ferritic materials, and (2) chromium-free nickel-alloy arc welds are at least ten times more susceptible to the deleterious effects of nitrogen than are mild-steel welds.

Carbon monoxide was second only to nitrogen as a potential cause of unsoundness in the high-nickel alloys investigated. Porosity first appeared in the

presence of about 4–5 per cent. of the gas and, as was the case with nitrogen, when the amount of gas in contact with the weld was increased to 7–10 per cent. severe damage was caused. Only the high-nickel materials which did not contain chromium were affected, and it was shown once more that mild steel was less sensitive than nickel-base alloys. Carbon monoxide is not regarded by the authors as a potential source of contamination with inert-gas welding, but its effects might be significant and should be taken into account when the metal-arc-welding technique is used with flux-covered electrodes.

The effects of oxygen were almost as damaging as those of carbon monoxide. Slight porosity was observed in the 'Monel' and nickel welds at a percentage similar to that of the latter gas (i.e., 4–5 per cent.), but when the amount of gas was increased to 10 per cent. porosity was found to be a little less than that caused by carbon monoxide. In atmospheres containing up to 10 per cent. of oxygen chromium-containing weld metals were again found to be free from porosity, but control welds in mild steel exhibited markedly greater susceptibility to damage by oxygen than by carbon monoxide.

Comparison of relevant data indicated that, as far as contamination with air is concerned, nitrogen is a much greater problem than oxygen. It is emphasized that though little porosity resulted from the presence of up to 5 per cent. of oxygen, even small amounts of the gas can be deleterious in other respects: oxidation of certain elements in the weld metal can, for example, have a disastrous effect on the properties obtained, and oxide crusts can interfere with production of satisfactory multiple welds.

Hydrogen was studied as a means of establishing its beneficial, rather than its deleterious, effects, since under certain conditions its presence can significantly improve the soundness of the weld: it is, however, concluded that the high levels of purity currently attained in the inert-gas shield render superfluous the use of hydrogen for this purpose.

Carbon dioxide has been suggested as a cheaper alternative to the shielding gases at present used for inert-gas consumable-electrode welding, but, in the case of high-nickel alloys, its effects are sufficiently adverse to discourage its use: (1) spatter is coarser and more abundant than with other metals; (2) CO_2 removes important deoxidizers and other additions; (3) it causes porosity when used with unmodified nickel or 'Monel'; (4) if used with alloys containing significant amounts of chromium, titanium or aluminium, it results in a heavy residue of oxide on the weld surface.

Porosity resulting from occlusion of gases may be minimized in two ways, which are often complementary: control of the welding variables so as to exclude the gases as much as possible from the arc atmosphere; modification of the weld-metal composition by addition of deoxidizers and gas-fixing elements. These two approaches to the problem are briefly discussed with reference to the high-nickel alloys. Emphasis is placed on the use of a short arc, effective shielding by the inert gas, protection from draughts of air, and addition of such stabilizing elements as titanium, manganese, silicon and aluminium.

Welding Chromium-Nickel Austenitic Steels

F. A. BALL: 'Welding Corrosion-Resisting Steels of the 18/8 Cr/Ni Type and Heat-Resisting Steels.'

Sheet Metal Industries, 1958, vol. 35, June, pp. 439–52; July, pp. 509–22.

This paper, in which reference is made to a *bibliography* of 50 items, is fundamentally a review of literature relating to the metallurgical factors involved in welding the 18–8-type chromium-nickel austenitic stainless steels and those of higher alloy content (for example, the 25–20 grades) which are used in heat-resisting applications.

In the first section the author is concerned primarily with the metallurgical principles which govern the production of sound welds. In this connexion consideration is given to the effect of composition on the microstructure of the weld metal, and to the significance of microstructure in relation to the occurrence of weld-metal cracking. The causes and prevention of 'weld decay' are also outlined. This information forms the background against which, in the second part of the paper, the advantages and limitations of various welding techniques are evaluated on the basis of their suitability for use with the austenitic steels.

By way of introduction to a discussion of methods used to determine the susceptibility of austenitic steels to weld-metal cracking, emphasis is placed on the desirability of ensuring the presence of a small proportion of free δ-ferrite in the weld metal. The rôles of the ferrite- and austenite-stabilizing elements present in the steel are outlined, and a brief résumé is given of the work leading up to the development of the Schaeffler diagram. Later modifications of this system are also discussed, and reference is made to several tests used to determine susceptibility to hot cracking, including the ring-test devised by Tremlett and the Tee test. Finally, dilution of the weld metal by the basis steel is considered, in the light of its effect on the ferrite content of a niobium-stabilized 18–13 steel.

The problem of 'weld decay' in stainless steels is covered by a short but comprehensive review of the conditions necessary for its occurrence, its causes, and methods used to overcome it. Discussion of the three methods generally employed to prevent this type of failure is followed by an outline of the precautions which need to be taken in welding the steels if the preventive measures are to remain effective. Particular reference is made to the behaviour of the titanium and niobium stabilizers on heating in various temperature ranges.

The section on weld decay closes with an evaluation of tests used to detect carbide precipitation at the grain boundaries, and brief reference is made to the incidence of 'knife-line' attack in stabilized steels. (In connexion with tests to determine susceptibility

to intergranular corrosion the reader may be referred to two new tests, described by STREICHER and WARREN in *A.S.T.M. Bull.*, 1958, Nos. 229 and 230, respectively; see abstracts in *Nickel Bulletin*, 1958, vol. 31, No. 8, pp. 247 and 248.)

The second half of the paper is concerned with the application of the normal fusion- and resistance-welding techniques to the austenitic steels, with details of procedures found to give best results. The scope of each section is indicated below.

Oxy-Acetylene Welding

Welding by this method is limited mainly to stainless steels of less than 0·1-in. (2·5-mm.) section, and, due to the deleterious effect, on corrosion-resistance, of carbon pick-up, is used mainly on steels intended for service in environments which are not severely corrosive. Notes are given on flux compositions, weld preparation and use of filler wires. Emphasis is placed on the advantages of niobium-containing filler wires, the dangers of using boron-containing fluxes and the importance of avoiding distortion.

Atomic-Hydrogen Welding

This technique is little used, but is particularly suitable for such applications as the production of stainless-steel tube from strip. It has the advantage of causing no carbon pick-up. Where a filler-wire is needed a titanium-stabilized steel has been found suitable, though loss of titanium occurs in the resulting deposit.

Metallic-Arc Welding

Metallic-arc welding is probably the process most widely used for joining austenitic steels, especially in construction of plant for the petrochemical industry. Some information is given on welding procedure, but the author's main concern is with discussion of the literature relating to the incidence and prevention of hot cracking in the weld metal.

Niobium-stabilized electrodes are preferred to those containing titanium, since the loss of niobium in the welding arc is appreciably less than that of titanium. Of the two types of electrode coatings available (lime fluorspar and lime titania), the former is preferred, as giving greater freedom from cracking, even in welds made under restraint.

In relation to hot cracking in austenitic steels, experience demonstrates the importance of composition; in particular, of the sulphur, phosphorus and niobium contents and of the carbon/silicon ratio. Reference is made to published results (derived from complex austenitic steels) from which it was concluded that weld metal cracked if: (1) it contained no δ ferrite; (2) the silicon exceeded 0·4 per cent. and the niobium content was more than eight times that of the carbon; and (3) the weld had been re-heated to a high temperature. These empirical findings form a background to a brief discussion of some of the mechanisms advanced to explain hot cracking.

Argon-Arc Welding

This process is well suited for welding of austenitic steels: the characteristics which make it so are outlined. The advantages of thoriated, *vis-à-vis* plain-tungsten, electrodes are mentioned. This process, which is replacing oxy-acetylene welding in the chemical and food-processing industries, can be used for austenitic steels down to a thickness of 0·008 in. (0·2 mm.). Recommended procedures cover the range 0·036–0·5 in. (0·9–12 mm.). Reference is made to the use of argon gas as a means of protecting the underbead in narrow-bore stainless-steel tubing, and to the effect, on the weld, of modifications in the composition of the argon-gas shield. Titanium-recovery in welding stabilized steels by this process is reported to be high. The section includes also some information on the welding of the austenitic steels by the consumable-electrode argon-arc process.

Submerged-Arc Welding

The method is applicable only to long straight seams or to circumferential joints in large-diameter cylindrical structures. Discussion of the process relates mainly to methods used to compensate for the high chromium loss which occurs during welding, due to reaction between the fluxes and the molten steel. The beneficial effects of using filler wires of higher chromium content are exemplified. It is pointed out that some doubt exists as to the validity of the Schaeffler diagram as guide to choice of composition when welding by this process.

Resistance Welding

is a technique particularly well suited to welding austenitic steel for service at elevated temperatures, and is used extensively in the fabrication of components for gas-turbine components. All the resistance-welding methods (with the possible exception of electric butt welding) are applicable to the austenitic steels, but the need for exact control of welding procedure is emphasized. In this connexion welding times, pressures and settings, electrode profiles, and joint preparation are discussed, and attention is directed to tests which may be used to verify the correctness of the welding setting. Since, by adjustment of welding details, it is possible to compensate for compositional differences, this variable is not of such importance as in fusion welding.

The paper ends with a brief note on the incidence and deleterious effects of sigma phase in the austenitic steels.

Annealing of Welded Stainless-Steel Tubing

J. S. ADELSON: 'Anneal Stainless Tubing for Corrosive Use.'
Iron Age, 1958, vol. 182, Aug. 7, pp. 83–5.

The author's aim is to emphasize the necessity of annealing stainless-steel welded piping and tubing to attain optimum resistance to corrosion. Low-carbon grades of the chromium-nickel 18-8-type austenitic steels (A.I.S.I. Types 304L and 316L) are commonly used for welded piping, and it is sometimes assumed that their low carbon content (used primarily to prevent intergranular corrosion) renders a subsequent solution-annealing treatment

superfluous. Carbide precipitation is, however, not the only, or nowadays even the main, cause of failure in stainless-steel tubing: intergranular corrosion attributed to the presence of δ ferrite formed during welding, stress corrosion following cold-working, and pitting are failures which have little connexion with carbon content or carbide precipitation.

The author describes cases of such failures, illustrating the protection derived from solution annealing in the range 1850°–2050°F. (1010°–1120°C.).

Brazing of Cermet Valve Components to 'Inconel'

G. M. SLAUGHTER, P. PATRIARCA and W. D. MANLY: 'Bonding of Cermet-Valve Components to Metals.' *Welding Jnl.*, 1958, vol. 37, June, pp. 249S–54S.

The success or failure of a fluid circuit operating at high temperatures may ultimately depend on the design of, and the material used for, the control valves. The materials employed for the valves are of particular importance, since not only must they possess sufficient rigidity to maintain their shape under the severe conditions involved, but they must also exhibit the corrosion-resistance and immunity to solid-phase bonding essential at such high temperatures. The results of previous investigations had indicated that cermet materials of the cemented-carbide type held promise of successful application as valve materials at service temperatures higher than 1000°F. (540°C.), provided that a satisfactory method could be found of attaching the cermet components to the metallic elements of the valve. Such a procedure has been successfully developed, at the Oak Ridge National Laboratory, in connexion with the brazing of cermet valve components to an 'Inconel' (nickel-chromium-iron-alloy) valve housing. The problems encountered and the techniques used are described in the present paper.

The chemical compositions of the cermets selected for study are given, together with their coefficients of thermal expansion in table I below. (The coefficient of thermal expansion of 'Inconel', over the range 0–1200°F., is $8 \cdot 5 \times 10^{-6}$ in./in./°F.)

Basically these cermets consist of titanium carbide and/or tungsten carbide (with small amounts of more complex carbides containing niobium and tantalum), bonded together by the nickel or cobalt constituents. The problem facing the authors resolved itself into two parts: (1) the difficulty of wetting the cermets sufficiently to achieve an effective brazed joint; (2) the necessity of finding some means of reconciling the difference between the coefficients of thermal expansion of 'Inconel' and of the cermets, so as to reduce the effects of contraction after brazing and prevent fracture of the joint or the cermet itself. Investigation of methods of overcoming these difficulties was carried out in three stages, the scope and results of which are summarized below.

(1) *Wetting Tests on the Cermets*

To determine the most suitable brazing material, each of the cermets was brazed to a nickel plate by means of various conventional high-temperature brazing alloys. The alloys and the relative degrees to which they wet the cermets are listed in table II. All the alloys adequately wet the cermet containing a high percentage of tungsten carbide (No. 6), but those containing large amounts of titanium were satisfactorily wetted only by alloys A, B, C and F. Bonding of the nickel-phosphorus alloy to the titanium-carbide cermets was greatly improved by pre-placing the alloy in the form of an electroless-deposit. Only the copper failed to wet cermet No. 5, which contained more of the minor carbide-forming constituents.

(2) *Development of Suitable Brazing Procedures*

As a means of minimizing the deleterious effects of the widely varying coefficients of thermal expansion

Table I

Composition of Cermets

Cermet No.	Composition								Coefficient of Thermal Expansion $\times 10^{-6}$ per °F. over the range 20-1200°F.
	C %	Ti %	W %	Ni %	Co %	Nb %	Ta %	Mo %	
1	15	58·3	—	—	18·7	7·5	0·5	—	4·5
2	15	58·3	—	18·7	—	7·5	0·5	—	4·3
3	13·1	52·1	—	30	—	4·5	0·3	—	5·3
4	13·1	52·1	—	25	—	4·5	0·3	5	5·3
5	6·7	6·7	68·5	—	10·75	1·7	5·4	—	4
6	5·4	—	80·6	—	11·75	0·6	1·4	—	3·1

of the cermets and the 'Inconel', a ¼-in. (0·6-mm.) thick layer of nickel was interposed between the two materials, on the assumption that when the composite was slowly cooled from the brazing temperature, the nickel would yield sufficiently to absorb the stresses involved. To counteract the brittleness of the nickel-base brazing alloys (which, with cermets 2, 3 and 4, were the main materials studied) the cermet was pre-wetted with the alloy and then copper-brazed to the nickel cushion, the copper acting both as filler metal and diluent. Subsequently it was found that the nickel could be effectively bonded to the titanium-carbide/nickel cermets merely by heating them, in contact with each other, in an inert atmosphere at a temperature (approximately 1350°C.) sufficiently high to form a liquid, alloying phase between the two materials. (Photomicrographs illustrating the microstructures of the bond are discussed.) Attempts to bond the titanium-carbide/cobalt cermets to the nickel cushion by this direct-contact method were unsuccessful.

(3) *Fabrication of the Composite Valve Component*

The stages involved in assembly of the valve discs (bonding of the cermet to the nickel layer and copper-brazing of this composite to the 'Inconel' shank) and of the valve seat (bonding of the cermet valve seat to the nickel cushion and copper-brazing of this sub-assembly to the 'Inconel' housing) are illustrated by photographs. To prevent excessive alloying during bonding of the cermet to the nickel, it was found necessary to machine observation ports in the nickel layer to detect formation of the liquid phase.

The titanium-carbide/cobalt cermet (No. 1) was brazed to the 'Inconel' by conventional techniques, using the palladium-nickel brazing alloy and substituting a 92-5-3 tungsten-nickel-copper-alloy cushioning layer for the nickel. The other cermets were successfully brazed by one or other of the brazing materials listed in table II.

Table II

Results of Bonding Tests

Brazing Alloy	Composition, wt. %										Brazing Temperature		Degree of Wetting *				
	Cu	Ni	Au	Pd	Cr	Si	B	Fe	P	C	°F.	°C.	Cermet No. 1	2	3	5	6
A	—	91·2	—	—	—	4·5	2·9	1·4	—	—	1920	1045	b	b	b	a	a
B	—	93·2	—	—	—	3·5	1·9	1·4	—	—	2050	1120	b	b	b	a	a
C	—	73·2	—	—	13·5	4·5	3·5	4·5	—	0·8	2150	1175	b	b	a	a	a
D	100	—	—	—	—	—	—	—	—	—	2050	1120	c	c	c	c	a
E	—	18	82	—	—	—	—	—	—	—	1830	995	c	c	c	b	a
F	—	40	—	60	—	—	—	—	—	—	2280	1250	a	a	a	a	a
G	—	70	—	—	20	10	—	—	—	—	2150	1175	c	c	c	a	a
H	—	90	—	—	—	—	—	—	10	—	1830	995	b	c	c	a	a

* a=good, continuous filleting and extensive spreading on the cermets;
b= fair, intermittent filleting but little spreading on the cermet; c=poor, wetting only at contact points.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

PRINTED IN ENGLAND *by* WIGHTMAN MOUNTAIN LTD.
WESTMINSTER, LONDON, S.W.I